INDUSTRIAL CHEMISTRY

AN ELEMENTARY TREATISE FOR THE
STUDENT AND GENERAL READER

BY

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WITH THE SUPPORT OF A LARGE
NUMBER OF COLLABORATORS

THIRD EDITION

TO THE CHEMICAL ENGINEERS
AND CHEMISTS
ALL OVER THE WORLD
YOUNG AND OLD
THIS BOOK IS
CORDIALLY DEDICATED

"Das ist's ja das den Menschen zieret
Und dazu ward ihm der Verstand,
Dass er im innern Herzen spüret
Was er erschafft mit seiner Hand."
Das Lied von der Glocke — Schiller

L'histoire des sciences et de l'industrie est là de tout ce qu'il faut
pour prouver que les idées les plus simples sont toujours
celles dont on s'avise le plus tard, et que les plus
vastes intelligences sont seules capables de les reconnaître,
tandis que les esprits médiocres manquent rarement de
s'égarer et de se perdre dans un dédale de combinaisons
vicieuses ou superflues.
Arthur Mercet

Men my brothers, men the workers, ever reaping something new
That which they have done but earnest of the things that they shall do.
Locksley Hall — Tennyson

Preface to the Third Edition

In the short span of four years which separate the present edition from the previous one, a number of front rank topics in our chemical world have been pushed into second place by newer ones. Thus the science of cracking petroleum fractions for gasoline is now an integral part of refinery practice; the new science, the one which engages everybody's attention, is the purification of lube fractions by solvent extraction, or the still newer one in the same field, the manufacture of gasoline from waste refinery gases and from natural gas by polymerization, preceded, if need be, by pyrolysis. In other fields, the inventiveness of the chemical engineer and chemist, driven frequently by economic or competitive necessity, has given us ammoniated superphosphates, sodium nitrate in pellet form, edible sugar from wood cellulose, architectural glass, still more solvents in the guise of chlorinated hydrocarbons, dyes for acetate silk, Neoprene, the new American rubber, and other items. New uses for standard products are exemplified by rayon cord for automobile tires, and by regenerated cellulose for sponges.

Less sensational but no less essential to the orderly progress of the industries are betterments and improvements represented by columbium addition to stainless steels in order to preserve their corrosion resistance even though heated; indium addition to silver to make it non-tarnish, the sodium phenolate gas washing process to remove sulfur and recover it; and several new instruments of control.

In the preparation of the present revision, all these newer developments have been considered, without however neglecting the standard, or, let us say, basic features of the industries, for these too must be included if the picture of the chemical technology is to be a faithful one. There has been included a greater number of figures for production, either in units of weight, or in money value, or both; and it will be noted that for many classes of goods, the figures have been broken down further than formerly. The purpose is to leave more and more the vague, and enter more and more into the precise, an instinct common to every scientist. The figures in such tables it will be further noted are mainly for 1935; there are no corresponding figures for 1936, for the reason, well known to many of my readers, that the Bureau of the Census compiles figures for the odd years only. The next figures will be for 1937, and will not be available until late in 1938.

In response to the request expressed in the earlier prefaces, many readers have been good enough to send me their comments and criticisms, much to the profit of the work. I hereby renew the request. All communications will be answered, as they have in the past, and be given con-

sidered attention. Such letters have come from nearby points, from the South, from the Pacific coast, from Sweden, from England, from Germany, from Russia, even from India. Along with the definite items exercised, the messages expressed goodwill, encouragement, and praise beyond the deserts of the work. My gratitude to these gentlemen will never be expressed adequately.

It has been my good fortune to enlarge the group of active collaborators by two, Mr. Raymond B. Stringfield, of Los Angeles, and Mr. W. Horak, of Hartford. Their contributions are duly accredited in the proper places.

Every request for information, addressed as they were to the Research Directors, managers, departments of manufacture, engineers, and chemists, was complied with; in most cases with such an abundance of materials that, to my infinite regret, only a portion thereof could be used in the text. In a very special way, my thanks are due to the several government bureaus and their officers: to Mr. L. V. Beck and associates, of the Bureau of the Census, Department of Commerce; to Dr. John W. Finch, Director, and to his associates, Bureau of Mines, Department of the Interior; to Dr. C. C. Concannon, Chemical Division, Bureau of Foreign and Domestic Commerce, Department of Commerce, and his local District representatives; to Mr. O. C. Stine, in Charge, Division of Statistical and Historical Research, Bureau of Agricultural Economics, Department of Agriculture, and to Mr. G. Burmeister, Senior Economist, of the same division; to Mr. A. L. Merz, Fertilizer Investigations, Bureau of Chemistry and Soils, the same Department; to Mr. Sidney Morgan, Secretary, United States Tariff Commission; to Mr. H. J. Zimmerman, Chief Statistician for Fats and Oils, Bureau of the Census; to officials in the Bureau for Plant Investigations; in the Corps of Engineers, War Department; in the United States Patent Office; in the Patent Office in London, in the Bureau of Patents in Ottawa; and to several other officials. These officials forwarded an abundance of exact information, supplemented in several cases by comments in letter form, and not only replied promptly but with that courtesy which may be considered characteristic of the real government officers.

In the preparation of drawings, I have again had the careful criticism and advice of my colleague, Professor Carlos Harrington, an expert in mechanical engineering.

Finally, I would like to quote an excerpt from the preface to the first edition (1928): "It has been the author's privilege to benefit by the rich experience of Dr. H. E. Howe, editor of *Industrial and Engineering Chemistry*....."

<div align="right">EMIL RAYMOND RIEGEL</div>

Buffalo, N. Y.
June 19, 1937.

TABLE OF CHEMICAL AND ALLIED MANUFACTURES

Relative Importance of Chemical and Allied Manufactures in the United States
the Census, Department of Commerce, supplemented by figures from the United

Motor car industry		
Vehicles	$2,391,056,395	
Bodies and parts	1,550,833,049	
Rubber tires, inner tubes	446,091,602	$4,387,981,046
Iron and steel		
Pig iron	358,145,499	
Cast iron pipe, fittings	37,870,081	
Gray iron, malleable iron	250,460,230	
Steel works, rolling mills products	1,931,318,220	2,577,794,030
Petroleum refining		1,838,621,913
Cotton goods (the 1929 figure)		1,524,177,087
Paper	711,793,299	
and pulp	167,208,261	879,001,560
Flour and other grain-mill products		853,219,061
Wool and hair manufactures		710,740,376
Cane sugar refining		377,214,442
Paints	158,481,925	
and varnishes	170,766,613	350,741,574
Leather, tanned, curried and finished		308,344,763
Druggists' preparations and patent medicines		291,733,473
Glass		283,925,061
Soap		239,152,130
Rayon and allied products		185,159,534
Clay products		177,918,949
Cottonseed oil, cake, meal, hulls and linters		177,738,000
...e		176,853,135
...lizers		140,386,112
...nufactured ice		128,609,687
Cement, Portland		120,417,129
Perfumes, cosmetics and other toilet preparations		119,446,172
Corn products; syrup	31,252,918	
corn sugar	10,975,634	
corn oil	13,833,996	
starch (90% from corn)	29,932,776	103,631,751
Beet sugar industry		95,159,801
Synthetic organic chemicals not of coal tar origin...............		86,334,188
Mirrors		68,767,653
Dry colors and pigments		66,257,992
Linseed oil, cake and meal		60,264,331
Photographic film, paper and plates		55,466,520
Safety glass (laminated glass)		53,282,938
Dyes .... 97,954,464 pounds		51,488,361
Gypsum products and building insulation		50,175,556
Compressed and liquefied gases		42,018,951

Allied Manufactures

for the year 1935; selected and arranged from figures supplied by the Bureau of States Tariff Commission, the Bureau of Mines, Department of the Interior.

Explosives		40,667,200
Disinfectants and insecticides, industrial, household, and agricultural		37,268,449
Tanning materials, natural dyestuffs, assistants and sizes		33,638,800
Baking powders, yeast, and other leavening compounds		32,340,648
Sulfuric acid, made and consumed at the plant	1,991,743 tons	
for sale, value of the	4,470,469 tons	31,907,469
Sulfur produced		29,367,200
Soda ash, made and consumed at the plant	637,224 tons	
for sale, value of the	1,871,335 tons	28,424,750
Glue and gelatin		28,161,033
Caustic soda, made and consumed at the plant	39,087 tons	
for sale, value of the	719,456 tons	28,104,631
Intermediates for dyes		26,074,279
Lime		23,323,071
Salt		21,088,641
Turpentine and rosin, from the gum only		19,232,724
Wood distillation and charcoal manufacture		15,970,917
Agricultural insecticides and fungicides		15,311,231
Boneblack, carbon black and lampblack		14,811,298
Synthetic resins, of coal tar origin		12,777,195
Phosphate rock produced		11,559,210
Acetic acid (as 100%)	98,697,347 lbs.	9,945,243
Medicinals, from coal tar		8,371,901
Chlorine, made and consumed at the plant	112,144 tons	
made for sale, value of the	207,159 tons	7,944,266
Carbon dioxide, liquefied	$4,528,449	
Carbon dioxide, solid "dry ice"	3,245,692	7,774,141
Boron minerals produced (borax, kernite)	272,967 short tons	5,381,560
Potash salts		4,993,481
Lead arsenate		4,129,464
Rubber accelerators		3,786,809
Butyl acetate	35,786,132 lbs.	3,675,656
Bromine	16,428,533 lbs.	3,483,239
Methanol (synthetic)	80,626,923 lbs.	3,402,643
Carbon bisulfide		3,309,644
Oleic acid		3,272,536
Hydrochloric acid, made and consumed at the plant	32,201 tons	
made for sale, value of the	54,889 tons	3,048,159
Stearic acid		2,776,396
Citric acid		2,768,377
Rubber antioxidants		2,674,792
Butyl alcohol	28,656,405 lbs.	2,656,405
Nitric acid, made and consumed at the plant	98,093 tons	
for sale, value of the	24,503 tons	2,142,817
Ethyl acetate		2,836,212
Calcium arsenate		2,302,844
Ether		1,613,993

WHAT "THINGS CHEMICAL" ARE WORTH:
Averages of sales for 1935, unless otherwise noted.

Bituminous coal (1934 figure), short ton	$ 1.75
Iron ore, at the mines, long ton	2.48
Salt, NaCl, short ton	2.66
Phosphate, Florida land pebble, long ton	3.41
Sulfuric acid, 50° Bé., chamber acid, short ton	6.40
Lime, short ton	7.44
Soda ash, short ton	15.19
Sulfuric acid, 66° Bé., short ton	15.50
Pig iron, long ton 1935	16.91
Pig iron, long ton 1936	19.10
Sulfur, brimstone, long ton	17.91
Sulfite pulp, unbleached, short ton	34.70
Chlorine, short ton	38.41
Caustic soda, short ton	39.06

Table of Contents

    (NOTE: The number preceding the running head for the right-hand pages indicates the chapter number.)

When the chemist thinks of the chemical industries he usually places sulfuric acid first. The manufacture of sulfuric acid is par excellence a task for the chemist; in its development, much pioneering, bold for those early days, was done. There will always remain linked to any discussion of sulfuric acid manufacture, the fine names of John Glover, Louis Gay-Lussac and George Lunge.

INDUSTRIAL CHEMISTRY

Chapter 1
Sulfuric Acid—Part I—The Chamber Process

Sulfuric acid is manufactured either by the chamber process or by the contact process. In the chamber process the acid made is rather weak, about 70 per cent H_2SO_4; the contact process produces 100 per cent acid and stronger grades containing the anhydride SO_3 in excess (the oleums). The chamber process is the older process; it is characterized by comparatively large reaction chambers made of sheet lead. In its original form, it presents the leisurely gait of the past century; it has maintained its place mainly because its product is concentrated enough and pure enough for the manufacture of superphosphate of calcium, a fertilizer. The contact process, on the other hand, produces the strong acid necessary for certain chemical reactions, such as those involved in the manufacture of dye intermediates. This process is characterized by the use of a solid "contact" substance, such as finely divided platinum, vanadium pentoxide, or ferric oxide.

Every year the chamber process is losing ground a little more, both in the number of plants, and in the tonnage of acid produced. There are still (1935) more chamber sets than contact plants, but the margin is now slim:

	1929	1935
Chamber sets	141	71
Contact plants	42	63

In production, chamber acid also retains its lead, but here again, only a small number of tons separate the two figures:

Chamber acid production, 1935	3,415,379 tons 50° Bé.	52.8% of total
Contact acid production, 1935	3,046,833 tons 50° Bé.	47.2% of total

The contact acid has gained steadily; in 1921, it was 25.2% of the total tonnage; in 1923, 27.6; in 1925, 29.2; in 1929, 36.2; in 1935, as listed above, not far from half the total. The trend is due to the development of extremely compact installation for manufacturing sulfuric acid with the new vanadium masses, and to the standardization of such plants. This development in turn has been favored by the availability

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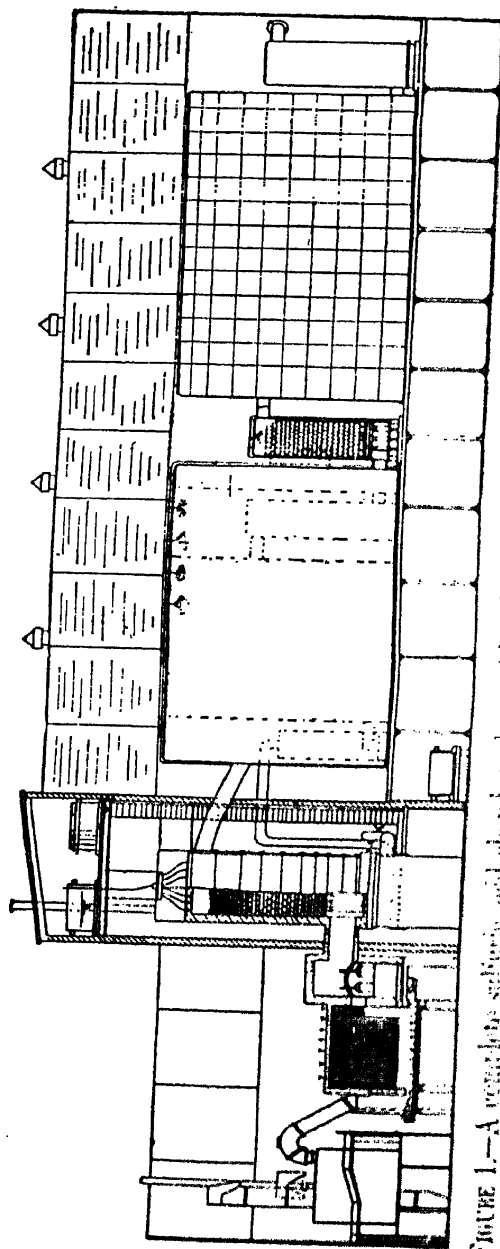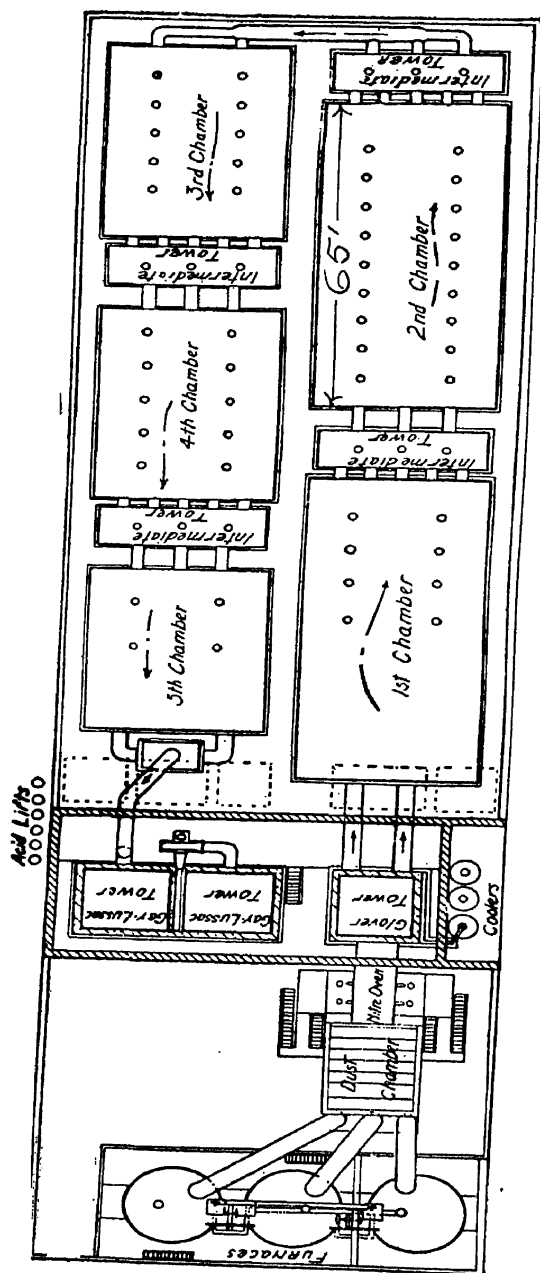
Figure 1.—A complete sulphuric acid chamber plant, with 3 furnaces, dust chamber, Glover tower, five rectangular chambers, the several intermediate towers, a Gay-Lussac tower, and fan, acid coolers. One-third of the acid made in the set, 90 tons per day, is lost in the Glover, the first four are 25 feet high, 6 feet wide, 28 feet long. (Courtesy of the Chemical Construction Corpn., New York.)

of brimstone at reasonable prices. Another reason for the greater growth of the contact process is that by that process, any strength acid, including the oleums, may be prepared with no other difficulty than diluting for the lower strengths; while by the chamber process, acid stronger than 55° Bé. can only be made by an additional operation, and oleums cannot be prepared at all. The trend, however, will be less pronounced in the coming years because of the ingenious advances in chamber construction and operation, described under "modern developments." In the operation of chamber plants, the potting of nitre is now almost obsolete, and the burning of the cheaper ammonia to produce the necessary oxides of nitrogen, permits a more intensive reaction; a slightly greater loss of nitric oxide can be tolerated. One pound of ammonia [NH_3] produces as much nitric oxide as five pounds of 100 per cent sodium nitrate.

A plant does not necessarily confine itself to one process,[1] but may operate both types plant, diluting the stronger contact acid with the weaker chamber acid to produce medium strengths.

The principal commercial strengths of chamber acid are:

50° Bé. acid (chamber acid)	62.18%	H_2SO_4[2]
55° Bé. acid (chamber acid)	69.65	"
60° Bé. acid (chamber acid, concentrated by heat)....	77.67	"
66° Bé. acid (oil of vitriol, concentrated by heat).....	93.19	"

A table for converting Baumé degrees to specific gravities will be found in the Appendix.

The strength of the acid is judged by a hydrometer test, with the hydrometer graduations in Baumé degrees (*see* Chapter 46). For the strengths up to 66° Bé. (93.19 per cent H_2SO_4), that is satisfactory; between 93.19 and just above 100 per cent H_2SO_4, the electrical conductivity is a reliable and convenient method. The oleums may be tested between 8 and 56 per cent free SO_3 with a hydrometer; below and above these figures, by titration. The commercial strengths of oleums are 15, 20, 26, 30, 45, 60, and 65 per cent free SO_3.

SET OF SULFURIC ACID CHAMBERS

In order to manufacture sulfuric acid by the chamber process, there are needed: (a) burners for lump ore, rotary burners for fines, or special burners for sulfur; (b) a Glover tower; (c) a set of chambers; (d) one or more Gas-Lussac towers; (e) several auxiliary devices. (*See* Fig. 1.)

A specific set with daily capacity of 17 tons of 55° Bé. acid per day is shown to scale in Figure 2, and will be described; it will reflect the older practice. With this plant as a basis, the important modern developments will be readily placed and appreciated.

(a) Lump Burners. The source of sulfur dioxide in this 17-ton set

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[1] A list of the sulfuric acid plants in the United States will be found in *Chem. Met. Eng.* **37**, 50 (1930).

[2] Taken from the table published by the Manufacturing Chemists' Association of the United States. The relation of Baumé degrees and decimal specific gravity is as follows: Baumé degrees = 145 − (145 ÷ specific gravity).

will be iron pyrite, FeS_2, a very heavy, yellow ore, also called fool's gold. In size it is two-thirds nut, one-third pea. There are 30 burners, mere fire-places, each 5 feet broad, 6 feet deep and 6 feet high, with cast iron grate bars and brick walls. Each receives a single charge of 1000 pounds per day. In order to start the ore, coke must be used, but once started, it supports its own combustion. Air is admitted under the grate bars, through a number of 2-inch holes which may be closed at will; the amount of air and therefore the percentage of sulfur dioxide in the "burner gas" is regulated here. The burner gas with all its heat passes through a flue to the nitre pot, and thence into the base of the Glover tower. The iron is left on the grate in the form of the dark red oxide, Fe_2O_3, which is discharged by shaking the grate. The reaction is $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$.
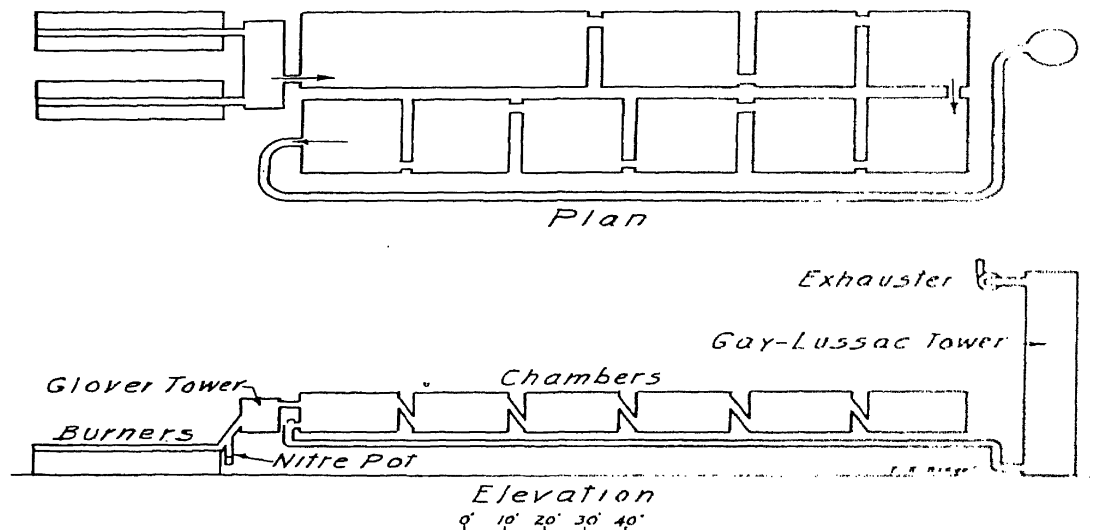
FIGURE 2.—Plant for the manufacture of sulfuric acid by the chamber process.

(b) Glover Tower. The Glover tower is a rather low rectangular box made of sheet lead supported by an outer steel frame and filled with quartz of assorted sizes. There passes down the tower the acid collected at the base of the Gay-Lussac tower, rich in nitrous fumes; and water which dilutes it and releases the dissolved nitrogen oxides. There passes up the tower the hot burner gas, carrying away the nitrogen oxides, and the water as steam. The Glover acid on issuing from the bottom of the tower passes through lead coils laid in running water, in order to cool it from 130° F. (54° C.) to 60° to 70° F. (15° to 21° C.). The cold acid is elevated by means of an automatic blowcase or acid egg to a small tank over the Gay-Lussac tower, from which it is fed gradually through a distributor and an elaborate system of small pipes, each with

a U-bend forming a seal, to every part of the packing in the tower. (*See* Fig. 3.)

(c) Chambers. The set has a first large chamber, with a floor 75 feet by 26 feet; a second chamber, 35 feet by 26 feet; and eight smaller chambers 26 feet by 28 feet.. The height for all is 14 feet. The walls, roof, and floor are of sheet lead, with the seams "burned" with lead, that is melted with the air-hydrogen blowpipe; the lead is supported on an outer frame of wood or steel.

(d) Gay-Lussac Tower. The Gay-Lussac tower is used in order to recover as far as possible the nitrogen trioxide gas which leaves the last chamber with the nitrogen and excess oxygen, and would otherwise be lost to the system. The tower is 70 feet high, circular with a diameter of 13 feet. It is made of lead supported by an outer steel frame and is filled with graduated quartz lumps, large at the bottom, smaller in size

FIGURE 3.—Blowcase for the elevation
of sulfuric acid.
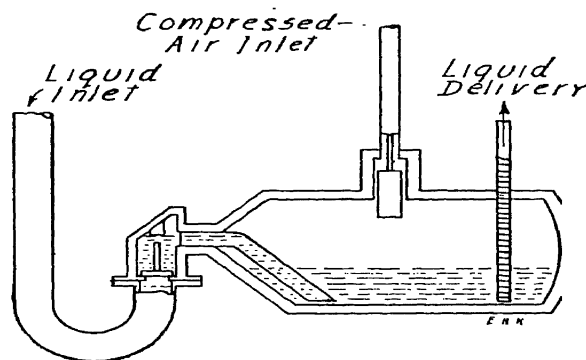
over that. There passes down the tower the cold Glover acid; there passes up the tower the gases from the tenth chamber; the descending acid dissolves the nitrogen oxides, and allows the other gases to escape. The absorption is never perfect. Nitrogen oxides, in the proportion of $NO + NO_2$, form a yellow gas which is soluble in cold 60° Bé. sulfuric acid; the strength of the solution after passage through the tower fluctuates between 1 and 2 per cent apparent N_2O_3; this is now the "Gay-Lussac acid"; when water is added to such a solution, the gas is liberated and passes out.

The marketable chamber acid is allowed to accumulate in the chambers, so that its level gradually rises. When the amount collected is sufficient, it is syphoned to a storage tank, or to a railroad car tank, ready for shipment. It is customary to use the chambers for the storage of the made acid.

Since 1918, acid-proof masonry has been successfully applied to the construction of Glover and Gay-Lussac towers.[3]

[3] "Recent developments in the manufacture of sulfuric acid," S. F. Spangler, *Ind. Eng. Chem.,* **21,** 417 (1929).

(e) Auxiliary Devices. These are a nitre pot, set in an enlargement of the flue leading the burner gases to the Glover box; acid eggs, or blowcases, into which acid is run by gravity, and forced up a long pipe to the desired point by compressed air; distributors, to divide the acid from a central pan at the top of a tower into a number of small streams so that all parts of the packing may be wetted. The nitre pot has been replaced by an ammonia burner, in many cases, and the blowcases are giving way rapidly to the small centrifugal pumps of special metal. In addition, a Venturi pipe to measure the flow of gas, a fan to pull the gases through the chambers and towers, and lead syphons and lines to transfer the finished acid to storage tanks.

In brief, then, the manufacture of the acid is as follows: Pyrite or sulfur is burned to produce sulfur dioxide; this oxide combines with oxygen and water, by the agency of nitric oxide, to form sulfuric acid. The Gay-Lussac tower is not needed for the reaction itself; it is a device for conserving the nitrogen oxides. The control of the reaction so that the loss of the costly nitre gas will be a minimum is the main problem.

In the cast iron nitre pot, the nitre was covered with Glover acid; the heat of the burner gas causes the gradual evolution of nitric acid which passes into the burner gas and there was reduced by sulfur dioxide to nitric oxide and dioxide. These nitric oxides, with more or less moisture, are commonly spoken of as the "nitre gas." The ammonia burner may be placed where the nitre pot was, and its gas delivered to the sulfur gas entering the Glover tower; a not infrequently selected place of entry however is after the Glover, just at the entrance to the first chamber.

The observations made by the "chamber man" in order to follow the reaction are: analysis of burner gas; temperature in the first chamber and in the last chamber; sulfur dioxide analysis in the last chamber; color of the gas, and fog, at the exit of the last chamber, observed by means of a glass globe set in the line; depth of the yellow color of the gas at the exit from the Gay-Lussac tower; specific gravity of the drips from a lead table placed inside each chamber and from two tables in the first chamber; titration of Gay-Lussac tower acid for nitrogen trioxide; gage reading at the Venturi meter; readings at the ammonia oxidation unit.

Travel of the Gas. The burner gas goes to the Glover tower, where it denitrates the mixture of Gay-Lussac acid and water; also it concentrates the acid, carrying the steam into the first chamber, so that in spite of the addition of water at the top of the Glover, the acid issuing from its base is as strong as the Gay-Lussac acid which was fed in. In addition to this steam, exhaust steam or atomized water [4] is admitted into the first chamber right over the inlet pipe, and into the subsequent chamber in a corresponding position. The reaction proceeds vigorously in the first chamber; its intensity is gaged by a thermometer or pyrometer. The steam or sprayed water is regulated so that the specific gravity of the acid is about 55° Bé. To be sure that "newly made" acid

is tested, sloping lead tables are built into the chamber with a connecting pipe to the outside, so that the "table drips" may be led, through a seal, to a hydrometer jar.

The gas then passes into the second chamber, through a short, wide pipe; then into the third, and so forth. In each chamber a heavy mist forms, which slowly settles, leaving the unchanged gases saturated with moisture. The droplets which settle are sulfuric acid with an amount of dissolved water depending on the amount of steam present. Too little steam causes a strong acid to settle, which on reaching 60° Bé. will dissolve the nitrous acid and form chamber crystals (nitrosyl sulfuric acid, $HNSO_5$). Too much steam may act also to remove nitrous acid by solution in the water of the weak acid, and this will dissolve the lead. The drips indicate in which direction the danger lies. In the last chamber the gas still should be about 2 per cent SO_2 and the temperature 80° F. (27° C.), if the first chamber is 115° F. (46° C.).

Composition of the Burner Gas and Fluctuations. The burner gas should have a composition of 8 to 11 per cent SO_2 by volume for the proper working of the chambers. Atmospheric air contains 20.8 per cent oxygen by volume; when using pyrite, 8 volumes are required for the formation of the sulfur dioxide, and 3 volumes to form iron oxide; hence there is left 9.8 per cent oxygen on the original volume; when using sulfur, 11 volumes of the oxygen may be used, with none wasted to the cinders, to give 11 per cent SO_2 gas. For the further formation of sulfuric acid, 4 volumes (or 5.5) of oxygen must be provided, plus a slight excess. The nitre gas is furnished by the Gay-Lussac acid diluted by water as it enters the Glover tower, supplemented by enough dry nitre plus Glover acid, or oxidized ammonia, to replace that lost to the atmosphere at the exit from the Gay-Lussac tower. If this normal loss alone were to be made good, the quantity would be constant, say 12 pounds an hour. But there are irregularities which cause greater losses over short periods. The most interesting of these is the diurnal fluctuation, due to the change in the temperature of the outside air from day to night; and what is more, it does not follow night and day closely, but lags about 6 hours behind. To maintain the proper intensity of reaction, the nitre during the cool period (night) must be decreased, while the nitre during the warm period (day) must be increased. Taking all the causes of loss of nitre gas together, a nitre gas consumption of 2 per cent of the nitre gas in the chambers including the Gay-Lussac acid is considered normal.

Aside from general unavoidable irregularities each set has its own peculiar defects due to its age. Leaks develop through the chamber walls, and to prevent a loss of gas, the fan speed is increased. As a result the gas is leaner, and other guiding temperatures must be settled as being the most advantageous. In other words, each set has its own "best" temperature.

The set described provides 10.1 cubic feet of chamber space for each pound of sulfur burned per day, if the ore delivers 38 per cent of its weight to the combustion air; this would be an average performance.

Sets are compared as to intensity of working by means of this figure; the effort is to make it small.

A chamber plant is very quiet; almost nothing can be heard except the overflow water from the acid cooling tanks, and the periodic escape of compressed air from the automatic acid elevators.

Brimstone-burning plant: Another chamber set in which *brimstone* is the source of sulfur dioxide will be described. Its burners are slowly rotating long cylindrical steel drums, with the long axis horizontal; the brimstone is melted. A regulated stream of air passes over the sulfur,
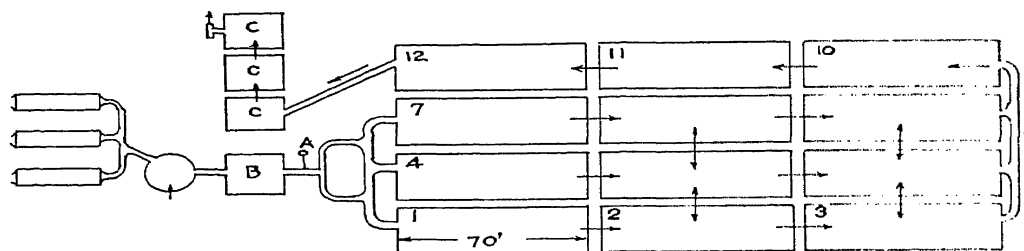
FIGURE 4.—Plan for the brimstone-burning chamber set. *B*, Glover tower, *C, C, C*, Gay-Lussac tower sections; *A*, ammonia burner.

keeping the blue flame going, and sweeping the combustion gases gently into a combustion chamber, a tall cylindrical tower set upright, which also receives the combustion gases of two more similar burners. Any entrained sulfur mist is burned here, with the aid of secondary air. The gas testing 11% SO_2 enters the Glover tower, then receives the nitric oxide from an ammonia burner, and passes into the chambers.

There are 12 chambers, each one 70 feet long, 24 feet wide, and 28 feet high; they are arranged in four groups of three chambers each. The gas enters numbers 1, 4, and 7 from the main header, and travels from each of these through two more chambers before reaching the return header; hence the gas has now swept through 9 chambers. The return header collects the partly reacted gas and sends it all through number 10, from there to number 11, then through number 12, thence to the Gay-Lussac, and finally through the fan to the exit. The operation is more intensive than in the previous set, the temperatures are higher, and the nitre gas loss between 3 and 4%.

The brimstone charge is 3000 pounds per hour; the ammonia burned is 500 pounds NH_3 per day; the yield is 4.85 pounds of 50° Bé. acid per pound of sulfur burned, an astounding figure, since the theoretical yield is 4.92 pounds. The space efficiency is 7.83 cubic feet per pound of sulfur burned per day. The temperatures for the first three chambers are 1st, 232° F. [111° C.]; 2nd, 232° F. [111° C.]; 3rd, 200° F. [93.3° C.]; while in the last three, they are 10th, 180° F. [82° C.]; 11th, 165° F. [73.89° C.]; 12th, 112° F. [44.4° C.]. The Gay-Lussac tower works at 80° F. [26.67° C.]; this tower is built in 3 sections standing side by side, the gas rising

up one section, down the second, and up the third. In cross-section, the sections are 20 feet square, and 35 feet in height; the packing is a silica brick. Water is introduced at the top of the Glover, in order to dilute the Gay-Lussac acid and liberate its nitre gas; this is supplemented by water sprayed directly into the chambers, through an atomizer with porcelain nozzle. All the acid made in the chambers passes through the Glover; the made acid is drawn off from there through coolers, to storage. 33 per cent of the acid is made in the Glover tower, and 20 per cent in the first chamber; the acid as it leaves the Glover is clear and colorless. Such a set runs very smoothly, and the labor requirements are small; one man to bring the sulfur to the hopper feeding the burners, another man for supervision and testing.

Ammonia Oxidation Unit. Instead of the nitre pot, an ammonia oxidation unit may be installed in order to supply the nitre gas required for the chamber operation. In such a unit, a mixture of air and ammo-

FIGURE 5.—A "Chemico" oxidation unit. 1, entry of ammonia aqua; 2, stripper; 3, warmed air; 4, exhausted liquor to waste; 14, condenser to hold back excessive moisture; 6, filter; 7, heat exchanger; 9, converter; 8, heater for the ammonia liquor; 12, outlet of nitre gas to the chambers. W, weak ammonia liquor.
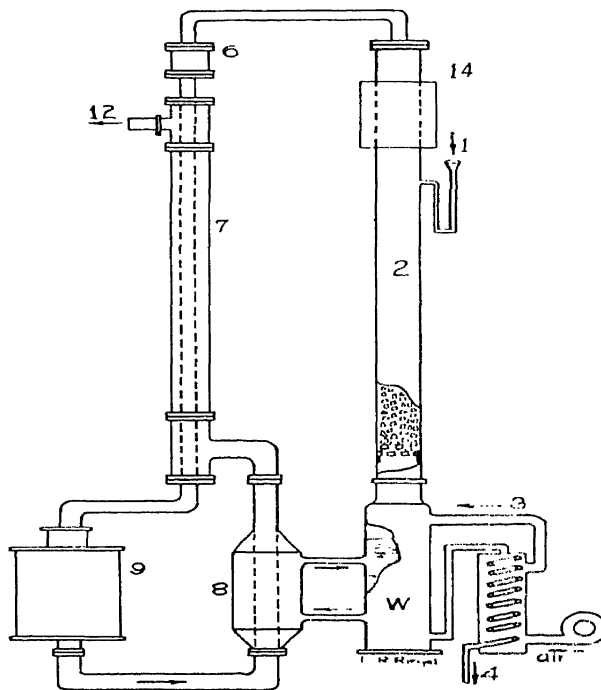
nia gas (11 per cent NH_3), preheated by the outgoing gases, passes through a fine mesh platinum gauze raised to red heat. In contact with the platinum, the reaction $4NH_3 + 5O_2 = 4NO + 6H_2O$, takes place, with an evolution of 214.2 Calories. This is enough heat so that with proper construction and preheating the gases no additional heat from an outside source need be applied.

The unit constructed by the Chemical Construction Corp., is shown in Fig. 5.[5] It is designed to receive aqua ammonia, rather than anhydrous ammonia; in the stripper column, warm air removes (strips) NH_3 from the solution; the mixed ammonia and air preheated in the interchanger 7, enter converter 9, where the reaction to form nitric oxide takes place. The outgoing gases reach first the heater 8, wherein the weak aqua ammonia is heated to boiling, then the heat exchanger 7, before passing out through 12 to the Glover tower. On the way there an oxidation of the nitric oxide to form a mixture of higher oxides takes place.

A picture of the converter, and further discussion of ammonia oxidation is given in Chapter 6 where the manufacture of nitric acid by ammonia oxidation is presented.

Another oxidation unit works on anhydrous ammonia directly.[6] The liquid anhydrous is vaporized in a coil heated by part of the outgoing gases, passes an oil filter and enters a mixer (a length of aluminum pipe) which also receives the preheated and filtered air required. The mixture, with a temperature of 250° C. [482° F.], enters the converter, whose contact material is an 80-mesh gauze of four layers, made of platinum-rhodium alloy (Baker number 750), and with strands .003 inch in diameter. At bright cherry heat, about 900° C. [1652° F.], the conversion is 95 to 96%. A unit burning 24 pounds of NH_3 per hour has a gauze cylinder 4 inches in diameter, and 7 inches high; its life is 6 to 12 months. The warmed anhydrous ammonia gas must pass an expansion valve, which is regulated by a Smoot regulator. The volume of air fed in by a separate blower, is filtered at its entry to the blower, and again after it is hot through a (Mid-West) filter having an oiled filtering surface for the retention of dust particles. The ammonia-air mixture is constantly analyzed and its composition indicated by a Ranarex analyzer (chapter 46). The operation of the oxidation unit is entirely automatic; the chamber man sights the platinum gauze for color, and reads the Ranarex; adjustments for different poundages to be burned are readily made.

SOURCES OF SULFUR DIOXIDE

The main source of sulfur dioxide is the burning of brimstone or of iron pyrite. In 1929, 66 per cent of the sulfuric acid made was from burning brimstone, 17 per cent from pyrite, and 17 per cent from smelter gases: for 1935, the figures are very similar. Before the war emergency, only 2.2 per cent of the acid was made from brimstone, the rest from pyrite or other sulfides, mainly imported. In 1935, 640,900 tons of 50° Bé. acid were manufactured from zinc and copper smelter gases. A burner for sulfur is described in Part II of this chapter. Acid for pharmaceutical use was always made from brimstone.[7] The sources of brimstone sulfur are discussed in Chapter 38.

[5] U. S. Patent 1,748,646.

[6] "Ammonia oxidation makes further gains in chamber plants," Theodore R. Olive, *Chem. Met. Eng*, **36**, 614 (1929).

[7] U. S. Pharmacopœia, Philadelphia, J. B. Lippincott, 1926.

Pure pyrite, FeS_2, contains 53.4 per cent sulfur. It is seldom found pure, but if it contains 42 per cent sulfur or more it is suitable for sulfuric acid manufacture. The arsenic content is important; less than 0.2 per cent arsenic is desirable for the chamber process, and imperative for the contact process.

Iron pyrite is imported from Spain (in 1935, 387,140 tons), which can supply the plants on the Atlantic seaboard advantageously. This source is less important now than before the war; an increasingly greater quantity of the native deposits is being exploited. Nearly all the States have iron pyrite rock; the production is of importance in New York, Virginia, Georgia, Alabama, and Missouri.

Pyrrhotite, Fe_7S_8, is more difficult to burn than pyrite; it is used in but one plant,[8] where the Herreshoff rotary furnace or burner, described below, handles this ore successfully.

The production of pyrite and pyrrhotite combined in the United States was 506,215 long tons, with a sulfur equivalent of 199,457 long tons, for the year 1935.

FIGURE 6.—A rotary shelf burner for fines; A, inlet for cooling air; B, outlet for cooling air, after it has swept through the rotating arms; C, inlet for combustion air; D, outlet for sulfur dioxide gas; E, inlet for the ore; F, outlet for the cinders.
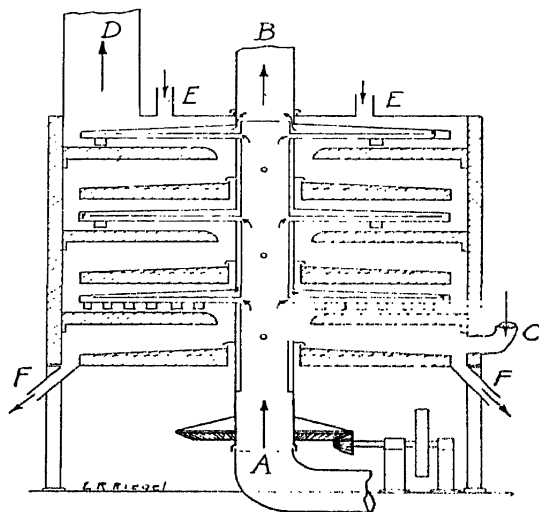
The Rotary Burner for Fines. Pyrite fines, the screenings from the lump ore, were at one time waste; the lumps were salable, while the fines, unavoidably formed in the process of mining and transporting, could not be used because they choked the fire in the lump burner. The fines were disliked also because of the considerable quantity of iron oxide dust which is carried by the combustion gas. They are now burned in automatic rotary shelf burners (*see* Fig. 6) with horizontal shelves and air-cooled raking arms (Herreshoff, Wedge). The spent cinders are discharged continuously from the lowest shelf. With the development of these

[8] The plant of the General Chemical Company at Pulaski, Va.

rotary burners, and of the Howard dust chamber which permits the fine dust to settle out and thus cleans the gas inexpensively, the fines have become as valuable as the lumps.

The Cottrell electrical precipitator [9] is successfully used for removing iron oxide dust from burner gas.

A method and apparatus for recovering sulfur dioxide from waste ferrous sulfate liquors has been devised.[10]

The purification of refiner gas or natural gas by the phenolate process (*see* chapter 14) leads to the recovery of vast amounts of hydrogen sulfide, which is now (1937) a source of sulfur dioxide for one acid plant, and will serve many more in the course of the coming years.

Flash Combustion Roasting of Iron Pyrite.[11] An entirely new way to burn pyrite, adapted primarily for the very fine powder obtained by the flotation process of treating the ore, has been developed. It consists in feeding the pyrite powder with a small supply of compressed air into a combustion chamber; secondary combustion air comes up from below. The ore burns as powdered coal does. The high temperature of 1000° C. (1832° F.) is allowed to develop, in order to prevent the formation of sulfur trioxide at this stage. Rapid cooling is provided by a fire tube boiler followed by a scrubbing tower.
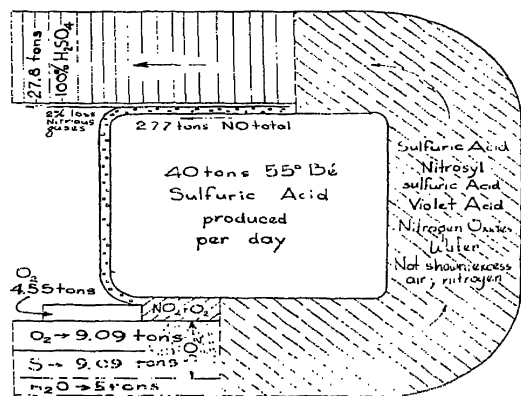
FIGURE 7.—Diagram of materials for a chamber plant which is to produce 40 tons of 55° Bé. sulfuric acid per day. The relations given are the theoretical ones, inasmuch as most plants almost reach these figures. Water of dilution amounting to 12.2 tons is not included in the diagram.

REACTIONS IN THE NITRIC OXIDE-SULFURIC ACID PROCESS

A set of reactions for the nitric oxide-sulfuric acid process has been given [12] by Ernst Berl, formerly a student and co-worker of George Lunge. The following cycle of reactions has been selected from that table, and

[9] Chapter 43.

[10] See flowsheet, *Chem. Met. Eng.*, 42, 699 (1935).

[11] Article by Horace Freeman, *Am. Inst. Chem. Eng.*, 26, 148 (1931); also article by W. M. Cobleigh, *Ind. Eng. Chem.*, 24, 717 (1932).

[12] "Studies of the lead chamber process," Ernst Berl, *Trans. Am. Inst. Chem. Eng.*, 31, 193 (1935); see also *Z. Angew. Chemie*, 44, 291 (1931), Berl and H. H. Saenger; *Z. anorganischen Chemie*, 202,113 (1931) and 208,113 (1932), by the same authors; and 208,124, Berl and K. Winnacker; *Z. Angew. Chemie*, 44, 821 (1932), W. J. Müller.

Reaction Mechanism: Sulfuric Acid-Nitric Oxide Process
$$SO_2 + \tfrac{1}{2}O_2 + H_2O = H_2SO_4 + 54 \text{ Cal.} \quad \text{Lunge-Berl}$$

1. $2NO + O_2 \longrightarrow 2NO_2$ homogeneous, in the gas phase; trimolecular
2. $SO_2 + H_2O \longrightarrow H_2SO_3$
3. $H_2SO_3 + NO_2 \longrightarrow (H_2SO_4)NO$ heterogeneous, in
    violet acid
4a. $2(H_2SO_4)NO + \tfrac{1}{2}O_2(NO_2) \longrightarrow 2SO_5NH + H_2O(NO)$ the
    nitrosyl   gas-liquid surface
    sulfuric acid
5a. $2SO_5NH + SO_2 + 2H_2O \rightleftarrows 2(H_2SO_4)NO + H_2SO_4$
4b. $(H_2SO_4)NO \rightleftarrows H_2SO_4 + NO$ homogeneous, in
5b. $2SO_5NH + H_2O \rightleftarrows 2H_2SO_4 + NO + NO_2$ the
5c. $SO_5NH + HNO_3 \rightleftarrows H_2SO_4 + 2NO_2(N_2O_4)$ liquid phase

represents the reaction mechanism for the chambers when operated at the usual pressure,[13] that is, one or two inches of water below atmospheric pressure. The reactions will explain themselves.

$$SO_2 + \tfrac{1}{2}O_2 + H_2O = H_2SO_4 + 54Cal$$

Sulfuric acid chambers operating at near-atmospheric pressure

$\tfrac{1}{2}O_2$ SO_2 $2H_2O$

2[H_2SO_4]NO+NO_2 $\longrightarrow$ 2SO_5NH+H_2O+NO
Violet acid   nitrosyl sulfuric acid

NO_2 $NO + \tfrac{1}{2}O_2$

2[H_2SO_4]NO+H_2SO_4 $\longleftarrow$ 2SO_5NH+SO_2+2H_2O

H_2SO_4

Nitrosyl sulfuric acid SO_5NH or SO_2.OH.ONO catalizes most rapidly when dissolved in 57.5% H_2SO_4; when dissolved in 75% acid, the nitrosyl sulfuric acid is not sufficiently labilized, and the reaction on the lower line takes place slowly.

FIGURE 8—Cycle of reactions in the sulfuric acid chambers, when operating at near-atmospheric pressure.

If this process is operated under pressure, the space yield rises; thus in the atmospheric pressure system, there are produced

at 1 atmosphere pressure,   18 pounds of 60° Bé. acid/hour/100 cubic feet
at 25 atmospheres pressure, 62,300 pounds of 60° Bé. acid/hour/100 cubic feet

[13] The theory of Rashig, in which nitrous acid is the working agent, is summarized in the Journal of the Society of Chemical Industry for 1911, p. 166.

or 3000 times more. The cycle of reactions for the pressure system is given in the figure below. There is no large scale installation which embodies the pressure process at the present time (1937); it offers however very large yields for a small-sized apparatus, and a new and promising application of the sulfuric acid-nitric oxide process. It will be noted that the nitric oxide does only a small part of the oxidation; most of it is done by the oxygen; hence the Gay Lussac tower would be small.

$$SO_2 + \tfrac{1}{2}O_2 + H_2O = H_2SO_4 + 54 \, Cal$$

Sulfuric acid-nitric
  oxide pressure process
    [Ernst Berl]

$\tfrac{1}{2}O_2$ SO_2 $2H_2O$

$$2(H_2SO_4)NO + \tfrac{1}{2}O_2 \longrightarrow 2SO_5NH + H_2O$$
                                    nitrosyl
                                    sulfuric acid

Violet
acid

$$2(H_2SO_4) + H_2SO_4 \longleftarrow 2SO_5NH + SO_2 + 2H_2O$$
$(\; NO\;)$

H_2SO_4

Under a pressure of several atmospheres, the oxidation of
the violet acid will be performed by the oxygen itself,
but not exclusively; to a certain extent, the oxidation
will be by NO_2, as in the atmospheric chamber process. The
liberated NO will be oxidised at an accelerated pace, due
to the higher pressure, so that even for that mechanism,
the higher pressure will increase production per unit
   chamber or cell space

FIGURE 9.—Reaction cycle in the sulfuric acid-nitric oxide pressure process; the pressure may be 10, 25, or 50 atmospheres.

MODERN DEVELOPMENTS IN THE CONSTRUCTION OF CHAMBER SETS

Mixing of the gases is essential; this has led to the construction of intermediate towers, of small cubic capacity, placed between the chambers. (*See* Fig. 1.) The towers are packed with stoneware rings, forcing intimate contact of reacting gases, resulting in a high production of acid.[14]

A great deal of acid is made in the Glover tower, perhaps 10 per cent of the total. The conditions in the cooler parts of the tower are

[14] See "The manufacture of sulphuric acid in the U. S.," A. E. Wells and D. E. Fogg. *Bur. Mines Bull.* **No. 184.** (1920), p. 108.

propitious; the temperature is high enough, water is abundant, the contact of sulfur dioxide, air, and nitrous acid intimate. This suggested the scheme of providing a second Glover tower, in which more acid might be made, before the chambers began their work. The Pratt converter is based upon this consideration. The first chamber is very large, comprising 75 per cent of the total chamber space. The reacting gases leave this chamber and enter a quartz packed "converter" tower in which intimate mixing is afforded and a considerable amount of acid made. From the tower the greater part of the gases are returned to a fan which feeds them into the first chamber again; a smaller portion passes to the second and third chambers.

The Anaconda Copper Mining Company has gone not merely a step farther, but all the way; its plant is all Glover tower, there are no chambers. The acid is made in acid-proof brick cells. The cooling is no longer by air, but by chamber acid which passes down the cell towers; this acid is then itself cooled in worms laid in running water, and used over and over again. The acid made is thus circulated ten times. Per pound of sulfur burned there is only 1 cubic foot of reaction space.

FIGURE 10.—Gaillard-Parrish sulfuric acid chambers, erected 1930, in London, England. Chambers are equipped with Gaillard turbo-dispensers for internal dispersion of precooled sulfuric acid. (Courtesy of Mr. Andrew M. Fairlie, Chemical Engineer, Atlanta, Ga.)
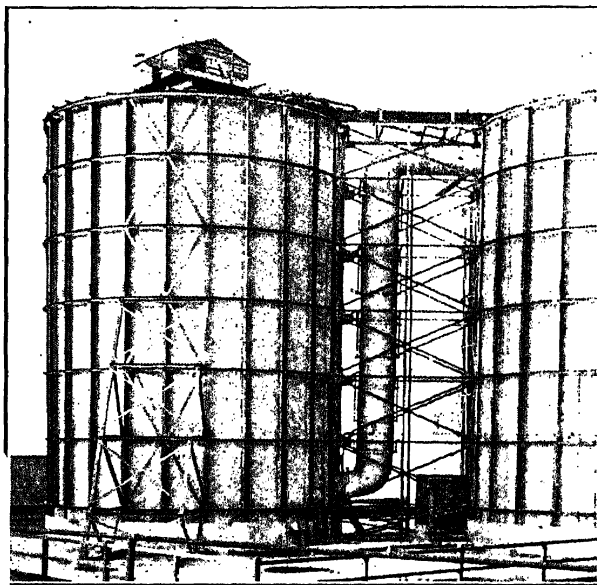
For a number of sound reasons, F. J. Falding has constructed chambers 75 feet tall, a single chamber followed by a special cooling tower taking the place of a number of smaller ones, with excellent results.

In order to use the gas from the copper blast furnaces for the manufacture of sulfuric acid, in spite of its fluctuation between 2 and 6 per cent sulfur dioxide, A. M. Fairlie has devised a method of control which

depends on the maintenance of desirable ratios between the sulfur dioxide in the gas entering the Glover tower and the gas in the first chamber. This is accomplished by potting varying amounts of nitre to meet the variations.[15]

The Gaillard-Parrish cylindrical sulfuric acid chamber [16] has the turbo-disperser of Gaillard, mounted at the top of the tower-like chamber devised by Parrish. (*See* Fig. 10.) The reaction takes place in the liquid phase; the turbo-blower delivers inside the tower finely divided cooled acid, which forms a fog, filling the chamber. It is on the surface of the droplets of this fog that the reaction takes place. A considerable volume of acid is withdrawn from the base, cooled in lead coils laid in cold water, and pumped into the turbo-disperser; this acid absorbs much of the heat of reaction, and thus favors its progress. The chamber is also cooled at the top.
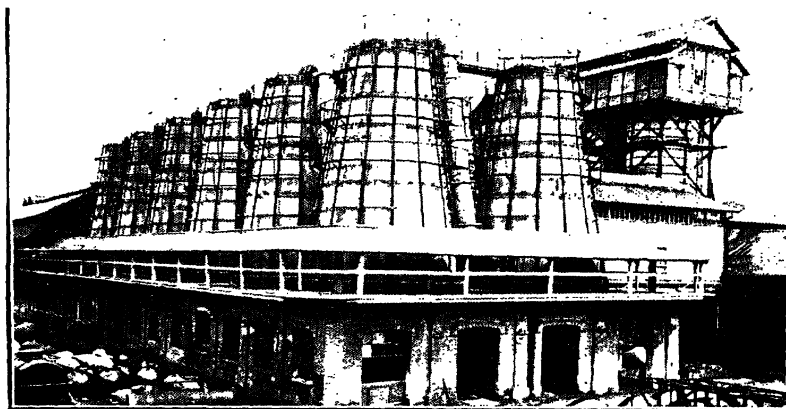

FIGURE 11. — Twelve Mills - Packard sulfuric acid chambers, truncated cone-shaped, outside water - cooled, free from enclosing structures; the Gay-Lussac and Glover towers are to the right. (Courtesy of Mr. Andrew M. Fairlie, Chemical Engineer, Atlanta, Ga.)

The Mills-Packard sulfuric acid chambers [17] are shaped like a truncated cone with the large side down; the average dimension would be 35 feet diameter at the base, 32 feet diameter at the top, and 50 feet for the height, with a cubical content of about 44,000 cubic feet (Fig. 11). The outside walls are water cooled by a curtain of water extending from the top all the way down. The removal of heat promotes the reaction, and in a small chamber space, more sulfur dioxide is oxidized than would be without the water cooling.

Both the Mills-Packard and the Gaillard-Parrish chambers are erected in the open, as the photographs in Figures 10 and 11 indicate, so that the expense of an enclosing building is avoided.

[15] Installed at the Tennessee Copper Co.; covered by U. S. Patents 1,205,733-4.

[16] Percy Parrish, "Liquid phase operation of sulphuric acid chambers gains significance in Europe," *Chem. Met. Eng.*, **36**, 68 (1929); *also* "Thermal aspect of liquid phase sulfuric acid production," **37**, 93 (1930).

[17] *Chem. Met. Eng.*, **37**, 468 (1930); *Trans. Inst. Chem. Eng. (Brit.)*, **5**, 42 (1927); *Chem. Met. Eng.*, **24**, 786 (1921); and British Patents 247,744 and 239,397.

A comparison of the efficiency of the more important chamber systems is given below.

TABLE 1.—*Efficiency of Sulfuric Acid Chambers System in Terms of Space.*

Chambers	Cubic feet of space per pound of brimstone burned per 24 hours (annual averages)	Cooled by
Rectangular	7.5–8.0	air
Mills–Packard	2.5–3.0	water
Gaillard–Parrish	2.5–3.0	cold-acid-circulated
Anaconda cells	1.0 (approx.)	cold-acid-circulated

Two other processes deserve mention, although neither is in successful operation at the present time; they are the Schmiedel process [18]
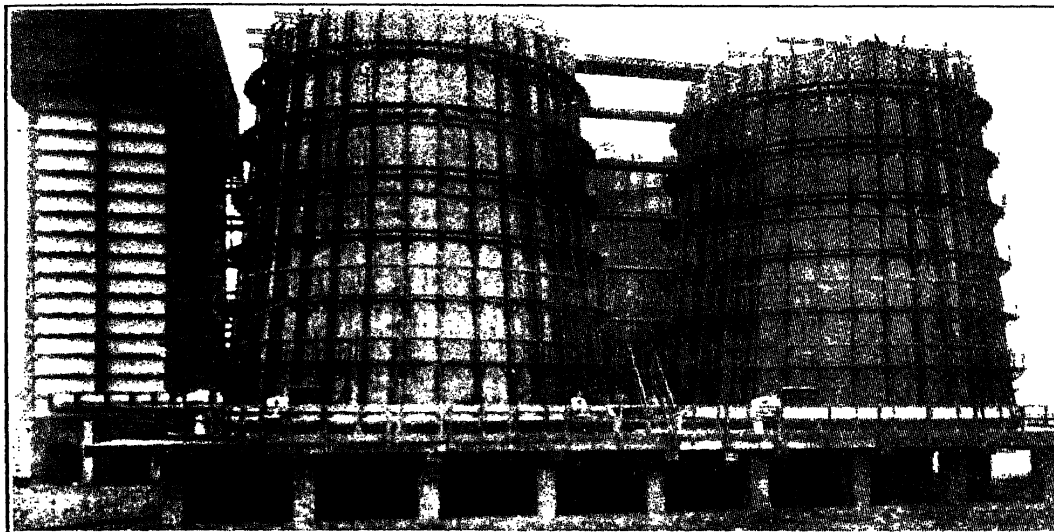

FIGURE 11a. A closer view of two Mills-Packard chambers for the manufacture of sulfuric acid by the nitric oxide process. (Courtesy of Mr. A. M. Fairlie, Atlanta, Ga.)

in which nitrosyl sulfuric acid is sprayed into the sulfur dioxide gas in order to provide as great a contact as possible; and the pressure process designed for a 4-ton per day production,[19] in which sulfur gas is introduced into a sealed tower 18 inches in diameter, which replaces the chambers. It is the rapid development in contact catalysis which has prevented the exploitation of these processes in the United States. The Schmiedel process is operated in some of the foreign plants.

Concentration. The chamber acid may be concentrated without expense for fuel from its normal strength of 55° to 60° Bé. by means of

[18] U. S. Patents 1,399,526 and 1,512,863.
[19] U. S. Patent 1,513,903.

lead pans placed over the lump burners. It may be concentrated to the still more valuable 66° Bé. acid with the aid of coal or oil fire. In the cascade system, the acid passes through a series of pans set stepwise so that each pan overflows into the next lower one; the hottest fire is near the lowest one which contains the strongest acid. The pans are glass, silica or duriron.

In the Chemico Concentrator [20] hot fire gases from an oil burner are passed through the acid, and remove water.

In another system, the gas from an oil burner passes up a tower 5 feet square and 39 feet high, packed with quartz, while the acid passes down the tower; water is carried out by the gases; they deposit such sulfuric acid mist as they may form with water in a wetted coke box. The capacity for such a tower is high, 24 tons of 66° Bé. acid per day.

It is not possible to concentrate chamber acid above 66° Bé. by heat, because above such strength the acid decomposes.

Prices. The prices for raw materials vary on account of market conditions and for other reasons. The price of the product varies also, depending upon market conditions, length of contract, and on specifications. The figures below are intended merely to indicate the usual price range.

Iron pyrite sells for $6 to $8 a ton, if the sulfur content is 45 per cent, hence the sulfur it contains costs 0.35 to 0.4 cents a pound. Brimstone is near 1 cent a pound. Chamber acid in 1935 averaged $7.83 a ton for 50° Bé. strength. Ammonia has been quoted as low as 5 cents a pound in carload lots, for the 100 per cent grade.

The cost of erection of a chamber plant is estimated at $3,000 per ton of 60° Bé. acid produced per day.

PROBLEMS

1. In the brimstone-burning chamber plant described in the text, the number and dimensions of the chambers are given, as well as the pounds of sulfur burned per hour. Compute the total chamber space available; extend the weight of sulfur burned to 24 hours, and find the space efficiency figure, then compare it with the figure in the text.

2. Find the pounds of 50° Bé. acid which may be made from 1 pound of sulfur. What is the percentage yield, if for each pound of sulfur, 4.90 pounds of acid are made?

3. Find the weight of water which must be furnished per day for the amount of acid made per day in the brimstone-burning set.

4. In the same set, if the nitric gas loss is 3 per cent of total nitric oxide in the set, including the Gay-Lussac acid, what is the total nitric oxide present?

5. Burning a pound of NH_3 to nitric oxide is equivalent to potting how many pounds of sodium nitrate, 100 per cent pure? Check the figure given in the text.

6. In the burner house, six burners of the rotating type receive 1000 pounds of brimstone each, every hour. The gas passes to 5 Mills-Packard chambers. How closely will the resulting space efficiency figure agree with the figure given in the table in the text, for such chambers?

7. Set up factors for changing sulfur, by weight, to H_2SO_4 100 per cent by weight, to 66° Bé. sulfuric acid, to 60° Bé., to 55° Bé., to 50° Bé. sulfuric acid. The percentages of H_2SO_4 for the several strengths will be found in the text.

[20] The Chemical Construction Corpn., N. Y.

8. Let the volume of gas from the burners be 8 per cent SO_2. In the first set described, in which the sulfur delivered to the gas is $30 \times 1000 \times 0.38$ per day, what is the weight of the sulfur equivalent, and of the sulfur dioxide produced, in pounds? What is the volume of the resulting 8 per cent SO_2 gas? The gram mole and the gram molecular volume in liters may be used, with a conversion figure taken from the appendix. For this purpose, assume that the gas is at STP. Let the 8 per cent gas be delivered through a 36-inch diameter line to the system; what is its velocity, in feet per second? To find it, compute the volume of 8 per cent gas served per second. If the gas has a temperature of $200°$ F. [$93.3°$ C.] when passing through the 36-inch line, what is its velocity?

9. What is the cost of materials for making 40 tons of $50°$ Bé. sulfuric acid per day, by burning brimstone, when the latter is bought at $17.91 a ton of 2000 pounds, plus 1 per cent for freight? The water is free.

10. The roof and the sides of the chambers are made of seven-pound lead, that is, of sheet lead weighing seven pounds to the square foot; the bottom is 10-pound lead. For the set of 12 chambers of the brimstone-burning plant, what is the weight of the lead required, and what is its cost, if the sheets as delivered are 6.5 cents a pound? An additional amount will be needed for the Gay-Lussac tower, for the Glover, and for the cooling tanks and their cooling coils at the foot of the Glover.
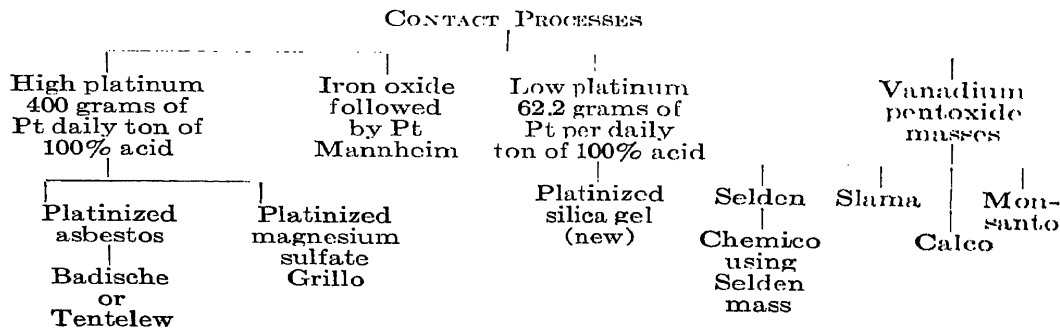
The difficult step in the manufacture of sulfuric acid by any process is the change of sulfur dioxide to sulfur trioxide. If sulfur burned to form at once the trioxide, there would have been no opportunity for many fine minds to exercise their inventiveness and ingenuity; but it burns to the dioxide only. In the chamber process, this is accomplished with the aid of nitrous acid; in the contact process, this same step is accomplished with the aid of a solid substance called the contact substance because when sulfur dioxide and oxygen are in contact with it, at the proper temperature, they unite to form the desired sulfur trioxide, which, with water, gives sulfuric acid.

Chapter 1—Continued

Sulfuric Acid—Part II—The Contact Process

The contact process became a firmly established industrial process at the turn of the century; until very recently, the contact material was mainly finely divided platinum on an asbestos carrier or on a calcined magnesium sulfate carrier. Of secondary importance was iron oxide as contact material. The situation has changed entirely since 1926, when the introduction of vanadium pentoxide as the contact substance took place. This less expensive agent is not used as such, but is always supported by an inert carrier such as diatomaceous earth, which does not fuse at the high temperatures |around 450° C. (842° F.)| employed. Its service has been so satisfactory that it may be estimated that for 1935, over half of the contact acid was manufactured with the aid of a vanadium pentoxide catalyst. For that year, the total production of the acid by all processes, including chambers, was 6,462,212 tons 50° Bé. acid, of which 47.2 per cent may be assigned to the contact processes. At the same time, platinum as contact agent has staged a revival, in the form of a very efficient platinized silica gel, which needs but a fraction of the metal previously required for the conversion of a given quantity of sulfur dioxide.

The various processes may be grouped together as follows:

CONTACT PROCESSES

High platinum 400 grams of Pt daily ton of 100% acid	Iron oxide followed by Pt Mannheim	Low platinum 62.2 grams of Pt per daily ton of 100% acid	Vanadium pentoxide masses
Platinized asbestos	Platinized magnesium sulfate Grillo	Platinized silica gel (new)	Selden / Chemico using Selden mass	Slama / Calco	Monsanto
Badische or Tentelew					

All the contact processes produce sulfur trioxide, the anhydride of sulfuric acid. It is a gas at any temperature above $45°$ C. ($113°$ F.) and atmospheric pressure. In water, it dissolves explosively, but in sulfuric acid of 98 per cent strength, it dissolves smoothly, and this acid is the common absorbent.

The reaction $2SO_2 + O_2 \rightarrow 2SO_3$, which takes place in the converter (under proper working conditions), takes place nearly to completion (to 97 per cent completion), at a temperature of about $450°$ C. ($842°$ F.). The catalyst may be platinum,[1] vanadium pentoxide, or iron oxide. At temperatures appreciably below $450°$ C. ($842°$ F.), sulfur dioxide escapes oxidation. At temperatures appreciably higher, the opposite reaction, $2SO_3 \rightarrow 2SO_2 + O_2$, takes place; the result in either case is the same, namely, the conversion falls below 97 per cent. The conversion figure is obtained by dividing the sulfur dioxide which is oxidized by the sulfur dioxide fed into the converter, and multiplying by 100. On closer examination, it is found that the rate of reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is only moderate at $400°$ C. ($752°$ F.), but it increases enormously with a rise in temperature. Thus at $500°$ C. ($932°$ F.) it is 40 times as great as at $400°$ C. ($752°$ F.). By rate of reaction is meant the amount of sulfur dioxide converted in unit time. The opposite reaction, $2SO_3 \rightarrow 2SO_2 + O_2$, is also accelerated by a rise in temperature, but becomes appreciable only at much higher temperatures. For example, at $400°$ C. ($752°$ F.) it hardly takes place at all; while at $550°$ C. ($1022°$ F.), its rate is high enough to produce a fair amount of the lower oxide. Hence it would be advantageous to provide a temperature of $550°$ C. ($1022°$ F.) to the gas as it enters the catalyst mass, and then after 80 per cent conversion or so, to cool the gas gradually, so that as it sweeps through the last portions of the mass, the temperature would be $425°$ C. ($797°$ F.). In this way a rapid reaction, and at the same time a high conversion should be attained.

The oxidation reaction is exothermic: $2SO_2 + O_2 \rightarrow 2SO_3 + 45.2$ Calories. This heat must be dissipated in the proper degree, in order to prevent excessive temperatures which would cause the reverse reaction $2SO_3 \rightleftharpoons 2SO_2 + O_2$ to proceed vigorously. More than enough heat is generated to maintain the apparatus at the proper temperature, and to preheat the incoming gases.

The catalytic reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ is a reversible reaction. It is desirable to drive it to the right. The law of concentration effect (the mass law) requires that the concentration of one of the factors (SO_2 or O_2) be increased, if it be desired to increase the formation of the product. By increasing the concentration of the oxygen, more of the product is formed, while at the same time, the sulfur dioxide is

[1] The honor of having discovered that platinum catalyzed the reaction to form the trioxide belongs to Peregrine Phillips, Jr., of Bristol, England (1831). Platinized asbestos was proposed first by the Englishman Jullion (1846).

nearly exhausted.[2]   The burner gas contains 8 per cent SO_2 which would require only 4 per cent O_2 for the reaction as written, but 10 per cent and more is always provided, an excess of 150 per cent or more, thus insuring a high conversion figure.

The conversion depends furthermore upon the temperature, the period of contact, that is, the relation between volume of mass and cubic feet of gas, and upon the activity of the mass.   The commercial installations illustrate all these factors.

The function of the contact substance is to adsorb at its surface the reacting gases; in the closer proximity which results, coupled with the high activation caused by the high temperature, the successful collisions are enormously increased in number and the speed of reaction is correspondingly raised.   In the case of platinum, surface adsorption is the only function; for the vanadium pentoxide (or other oxides), it is more likely that the various oxides of vanadium do take part in the action, the higher oxides giving up oxygen, but continually reformed by the incoming oxygen, so that they are found unchanged after the reaction.   It may be said, therefore, that the contact substance in any process is unchanged after a period of years.   Commonly, the life of a mass is taken to be 10 years.   The subject of poisoning is presented after the plants have been described.

Additional discussion on catalytic reactions will be found in Chapter 25.

The Chemico Process with Vanadium Mass

A Chemico contact sulfuric acid plant of capacity of 17 tons 100 per cent H_2SO_4 a day will be described as typical of the most advanced

[2] At any one definite temperature within the range concerned, and in the presence of the catalyst, an equilibrium between the gases SO_2, O_2 and SO_3 will be attained, provided enough time is allowed.   The value for the equilibrium constant in the formula

$$K_p = \frac{(PSO_3)}{(PSO_2)(PO_2)^{\frac{1}{2}}}$$

using partial pressures in atmospheres, for the temperatures observed in practice, is:

Temperature	K_p	K_c
400° C.	467	109,700
425	255	61,000
450	145	35,300

Expressing the constant in terms of mols per cc., for the same reaction, the values listed under K_c are obtained.

The reader will please note that the expression applies to the reaction $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$, not for the reverse reaction, nor for the reaction written with twice the number of molecules; for the latter the value of the constant will be the square of the above values; for the former, the reciprocal.

It may be well to point out that it is the constant K which does not change, while the absolute amounts of the three gases may be altered.   If the concentration of oxygen is increased, the value of (PSO_2) must decrease, to maintain the value of K, assuming the change in (PSO_3) to be relatively small.   This is what happens when a 100 or 200 per cent excess oxygen is provided. K may also be expressed in terms of the constants of the reaction rate, k_1 for the forward reaction, k_2 for the reverse reaction, then $K = \dfrac{k_2}{k_1}$.

earliest researches on the value of the equilibrium constant, specific rate constant, and optimum temperature were those of Knietsch, which formed the basis for the original contact ...ith platinum, the "Badische" process.   A summary will be found in *Berichte der deutschen chemischen Gesellschaft*, v. 34, p. 4093 (1901).   Knietsch used flowing gases; more recently W. K. Lewis also used flowing gases, and reconsidered Knietsch's data as well as set up new values by experiments: Influence of reaction rate on operating conditions in contact sulfuric acid manufacture, *Ind. Eng. Chem.*, 19, 830 (1927) and 17, 593 (1925), where references to the work of Bodenstein on quiescent gases will be found.   See also "reading references."
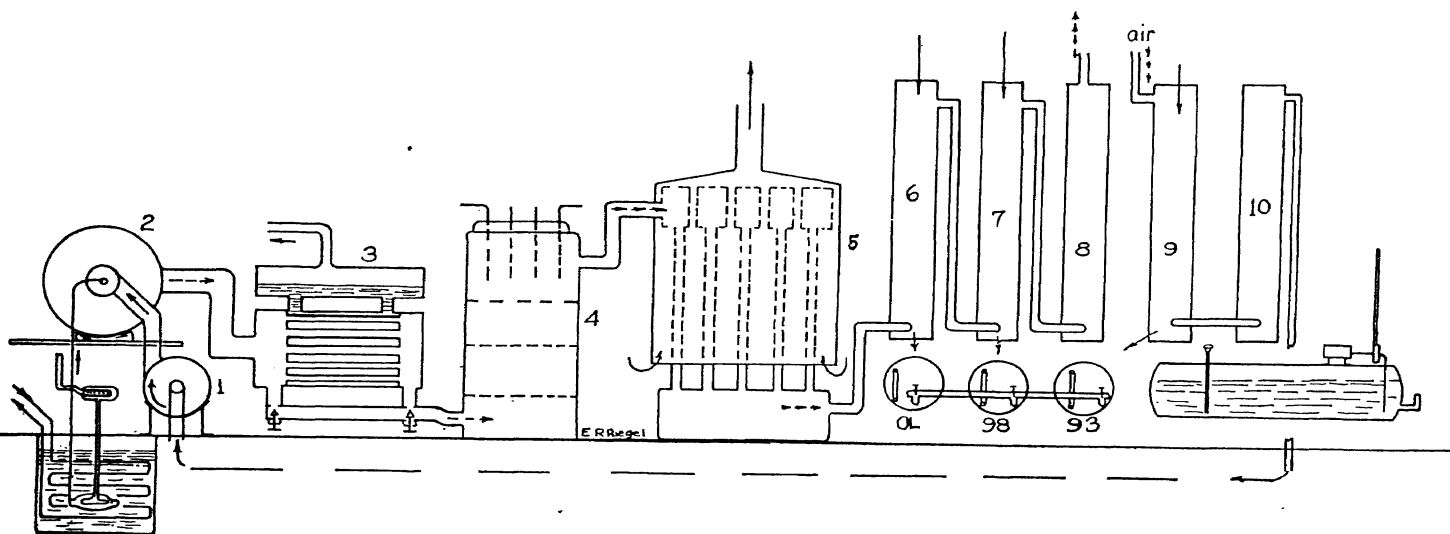
FIGURE 12.—Diagrammatic flow-sheet for the Chemico sulfuric acid contact process, with vanadium pentoxide mass. 1, fan; 2, sulfur burner with melted sulfur tank below; 3, boiler; 4. converter; 5, natural draft cooler; 6, oleum tower; 7 and 8, 98% acid tower; 9 and 10, towers for drying combustion air. (Sketched through courtesy of the Eastman Kodak Company, Rochester, N. Y., and the Chemical Construction Corpn., New York.)

practice of the present period. It has many features which will be welcomed by the student, particularly two: simplicity and compactness. The simplicity of the plant results in large part from the use of brimstone sulfur as raw material; all auxiliary apparatus for cleaning burner gas, from the combustion of pyrite, is absent. Sulfur is melted, burned with air in the special spray burner, the combustion gases, with 7 or 8 per cent SO_2 are cooled by passing them through a waste heat boiler, and then enter the converter. One important purification is provided, however, and that is: the air is dried. The drying avoids a number of difficulties, such as corrosion of parts and mist formation. *The compactness* of the plant is such that it is housed complete in what might be a good-sized room, with five towers just outside.

The diagrammatic flow-sheet in Figure 12, drawn from an actual plant, gives the sequence of operations. Melted sulfur is forced through the spray burner tip by a steam-driven turbine, submerged in the sulfur. The pressure on the melted sulfur is sufficient to drive it through a spiral cut in the adjustable valve rod (needle valve type), so that it acquires a rotary motion and is discharged into the burner in a wide arc. The dried combustion air (at 106° F. or 41° C.) enters at the sides of the burner tip. The burning chamber for burning 5 (or 6) tons of sulfur per day is a cylinder lying on its side, 7 feet high and 17 feet long. It is of steel, brick-lined, with alternately hanging arches and bridges as baffles. The gases leave the burner at 771° C. (1490° F.), and pass through the water-surrounded tubes of a boiler.

On leaving the latter, the gases, with temperature 304° C. (580° F.), enter the converter, which carries the contact mass in two layers: 1800 pounds in the lower layer, 1200 pounds in the upper. One pound of the catalyst occupies one liter volume. The internal arrangements are as shown in Figure 13, which also gives the temperature for the gas (and mass) at various levels. The lower layer is cooled by the entering gases which reach the top of the risers, and are deflected downward by means of the slender thimbles inverted over them. In the upper layer, the mass is cooled by a current of cold air. In the latest form of Chemico converter, shown further in the chapter, the upper layer is not cooled.

On entering the bottom mass, the gases are 493° C. (920° F.); 6 inches above the lowest layer, the maximum temperature is met, 593° C. (1100° F.). On leaving the bottom mass (upper portion) the gas is 482° C. (900° F.); the temperature in the top layer, where the conversion is completed, is 438° C. (820° F.).

The sulfur trioxide gas produced is cooled by air draft, and enters the absorption towers, about 20 feet high and 4 feet in diameter, packed with 3-inch "spiral rings." The gas travels through the three towers in series. In the first tower, 20 per cent oleum is made; the delivery from the tower enters the oleum collection tank, and is recirculated. With recirculation, a smaller tower is sufficient; instead of a single pass down a large tower, many passes down the smaller tower provide the same absorption. In the second tower, 98 per cent H_2SO_4 acid is made, also

with recirculation; while in the third, 93 per cent acid is made which exhausts the gas of its sulfur trioxide. The waste gas is discharged through the stack.

Two supplementary towers fed with 98 per cent acid are connected to the suction side of the blower and remove the moisture from the combustion air.

The recirculation of the acids is by means of self-priming, special metal centrifugal La Bour pumps of very small size, set just above each tank; the capacity is 50 gallons per minute at 1750 rpm. (see Chapter 41).
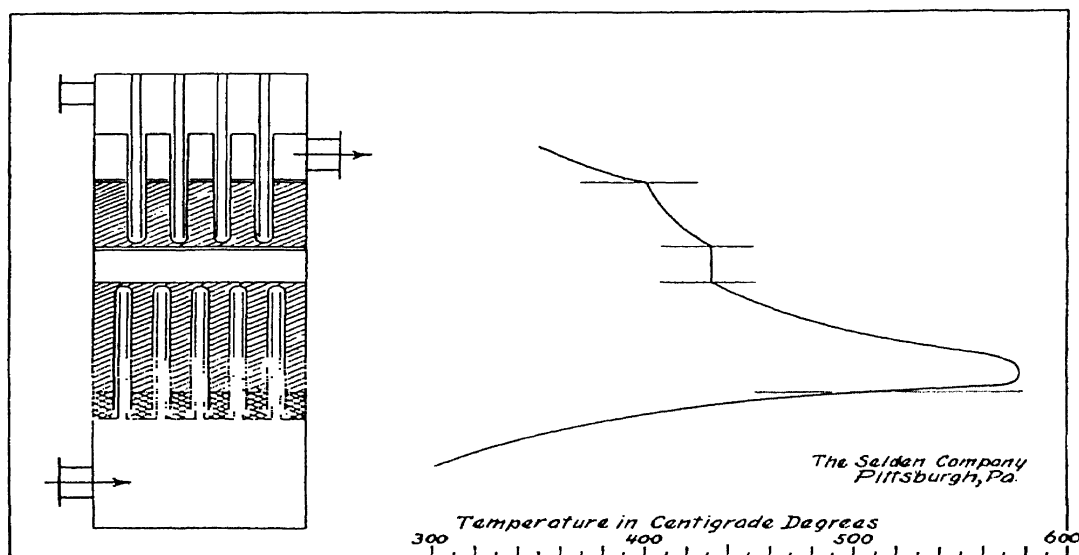

FIGURE 13.—The temperature for gas and mass at various levels in the "Selden" vanadium pentoxide packed converter for sulfur trioxide formation.

The charge of sulfur is 500 pounds every hour, dumped into the sulfur melting tank. The acid made is delivered from the several tanks periodically, to other departments or to storage tanks.

Control of Operation. The plant is practically automatic. No labor is required except for charging the sulfur. The operation of the sulfur burner is controlled by means of the temperature of its exit gas which affects a resistance pyrometer; should the temperature drop, a Wheatstone bridge is unbalanced, and the current which can flow actuates a control which in turn allows more steam in the turbine, so that more sulfur is delivered to the burner. The volume of air is set. If the temperature of the exit gas rises, the opposite action results in decreasing the steam on the turbine.

The 98 per cent acid is controlled by measuring its electrical conductivity, and this is checked periodically by the "heat rise" test, as

ollows: 200 cc. of 105 per cent H_2SO_4 at temperature T_1, and 200 cc. f the acid to be tested having temperature T_2, are poured together and 1e temperature of the mixture, T_3, noted. The value of R is found from 1e expression

$$R = T_3 - \frac{(T_1 + T_2)}{2};$$

Table 2 gives the percentage of the acid tested.

TABLE 2.—*Testing of 98 Per Cent Acid for Strength by the Heat Rise Test.*

R		Per Cent H_2SO_4	R		Per Cent H_2SO_4
2°	C.	99.9	18	C.	97.5
4	....	99.5	20	....	97.3
6	....	99.3	22	....	96.9
8	....	99.0	24	....	96.4
10	....	98.7	26	....	96.2
12	....	98.4	28	....	96.1
14	....	98.1	30	....	95.8
16	....	97.8			

The strength of the 20 per cent oleum and of the 93 per cent acid is tested by a hydrometer.

The pressure of the air on inlet to burner is 55 inches of water, on the gas entering the converter 43 inches, leaving the converter 28 inches, hence a differential of 28 inches due to the converter mass. Should this differential increase, it would mean that the mass was dirty, or had become plugged in some other way.

Chemico Converter, full size. A Chemico converter for a plant having a capacity of 40 tons of 100 per cent H_2SO_4 per day, embodying the latest design, is shown in Figure 14. It will be noted that it has but one set of tubes, in the lower mass; the entering gases cool the mass, then pass through it, undergoing a preliminary conversion of about 85 per cent. The tubes and thimbles are longer than in previous designs; also the thimbles are "calorized"[3] in order to increase their heat resistance. The packing of the mass is as follows: Over the perforated plate, a wire netting is placed, which carries ½-inch quartz pebbles to a height of 2 inches; over these, the catalyst is placed, uniform in size. The conversion is completed in the upper layer, which receives no cooling. Other details and dimensions may be obtained from the sketch.

Other Processes. An installation using brimstone sulfur with the Monsanto vanadium has a compactness[4] similar to that of the Chemico process and an operation similarly neat. The low-platinum silica gel mass lends itself readily to similar installations.

The Various Catalyst Masses. The catalyst masses of modern type best known in the United States are listed in Table 3, with their

[3] A process patented by the General Electric Co. Aluminum is driven into the surface of mild steel, by heating, forming an aluminum alloy.
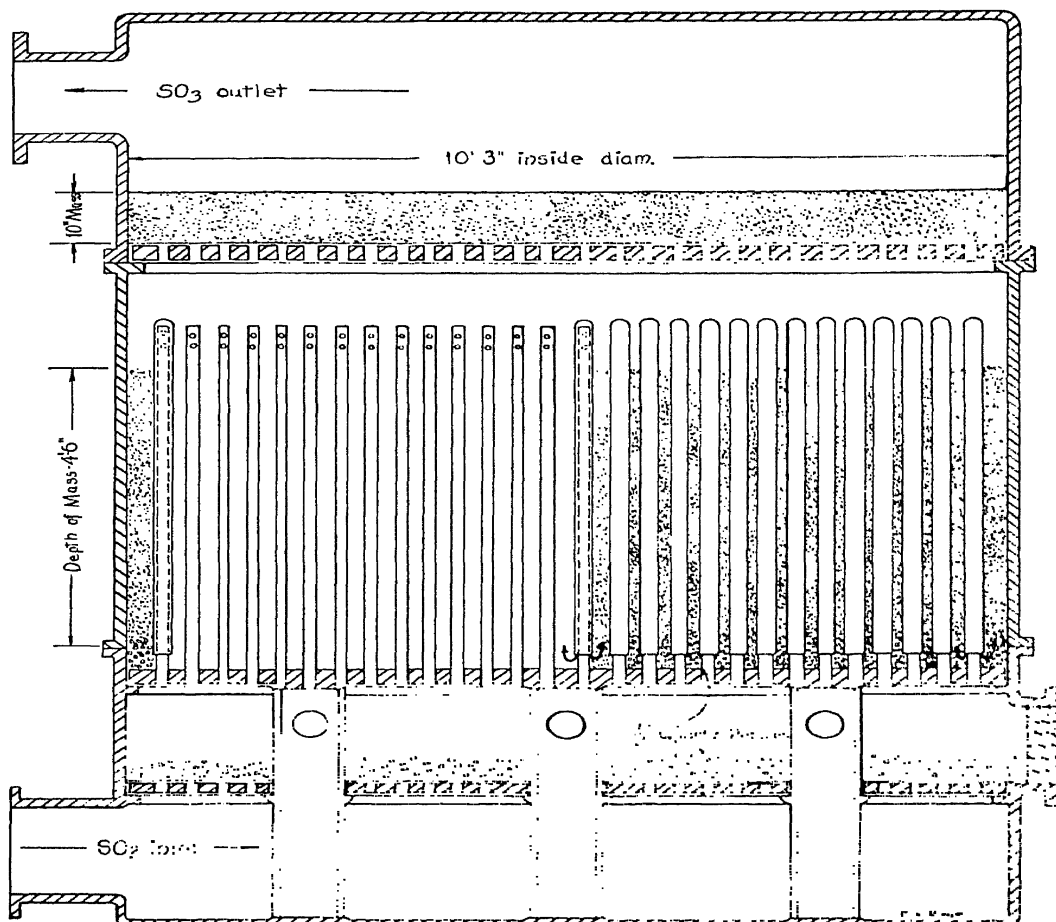[4] Daniel S. Dinsmore, *Trans. Am. Inst. Chem. Eng.*, **26**, 158 (1931).

FIGURE 14.—The most recent form (1933) of the Chemico converter with vanadium pentoxide mass. It is circular in cross-section, has 716 thimbles and tubes, and a capacity of 40 tons per day. The thimbles and contact mass for the left half of the drawing have been omitted, in order to show the inner risers through which the gas enters. (Sketched through courtesy of the Chemical Construction Corpn., New York.)

density, efficiency, and appearance. The efficiency is in terms of the daily pounds of sulfur as 8 per cent SO_2 converted per liter of catalyst mass.

Preparation of the Selden Mass. The vanadium pentoxide mass known as the Selden mass, developed by Dr. Jaeger, and used for the Chemico installation just discussed, is made as follows: [5]

[5] Taken from the court findings, Federal District Court for the Western District of Pennsylvania, in the case of the General Chemical Co. vs. the Selden Co.; the former claimed infringement of its patent 1,371,004 (Slama and Wolf). The court decided that the Selden Co. was not infringing. June 17, 1932. Since then the case has been reopened and is now in the hands of a special Master (early 1937).

"A." A solution of potassium silicate is sprinkled on diatomaceous earth; and the wetted particles are mixed by shoveling and raking.

"B." Potassium aluminate is made from potassium hydroxide and alumina, in the form of a solution.

Two equivalents of "B" are sprinkled on 5 equivalents of "A," and well mixed. The potassium aluminate and potassium silicate form a zeolite, of jelly-like consistency.

"C." Ammonium vanadate solution (3 equivalents) is added to potassium aluminate (1 equivalent) and potassium hydroxide, forming a thick gelatinous suspension which can just be poured; it contains a complex vanadium compound.

"C" is poured onto the soft zeolite-coated diatomaceous earth, mixed only slightly, without penetration. The lumps which form are compacted, screened, a small amount of stearic acid added (as lubricant) and formed into pellets ¼ inch in diameter. The pellets are calcined or sulfated by heating in a current of 1 per cent SO_2, gradually raising the heat to 500° C. (932° F.) and increasing the proportion of sulfur dioxide. After calcination, the pellets are cooled in a current of air, and are packed in air-tight containers, for shipment. This is the finished catalyst, ready for the converter.

During the calcination, vanadium pentoxide is formed, but remains in intimate contact with the other constituents of the pellets.

TABLE 3.—*SO₂ to SO₃ Catalyst Masses.*

	Apparent density of mass	Daily pounds of sulfur as 8 per cent SO_2 gas converted per liter of catalyst mass	Appearance
Selden mass, V_2O_5	0.46	5	Light greenish-yellow tablets ¼″ diameter
Monsanto mass, V_2O_5	0.56	5	Light green half-cylinders ⅜″ length
New platinized silica gel	0.50	5+	Brown sand-like granules ¼″ in length

For these three masses, a volume of catalyst fluctuating between 125 and 175 liters will be required for the production of a daily ton of 100 per cent H_2SO_4.

Badische Mass. A vanadium mass successfully used by the Badische Anilin und Soda Fabrik, in Germany, is made as follows: 316 parts of kieselguhr are mixed with a solution of 50 parts ammonium vanadate and 56 parts potassium hydroxide; enough water is evaporated to allow the formation of granules. These are heated at 480° C. (896° F.) in 8 per cent SO_2 gas, then cooled in a current of air.

Platinized Silica Gel. Platinum was the original contact substance for the sulfur dioxide oxidation. It was dispersed on asbestos fibers or on magnesium sulfate crystals followed by a careful calcination. Both these masses were and are efficient, but they contain so much platinum, in terms of sulfur treated, that new installations would not be able to compete with the vanadium masses.[6] A smaller amount of platinum dispersed on silica gel, with a final density of 0.7, was superior to platinized asbestos or platinized magnesium sulfate, and a new silica gel mass, of more recent introduction, is a further improvement in the same direction. In comparing vanadium and platinum masses from the standpoint of cost, it must be remembered that 90 per cent of the platinum value

[6] This is disputed, on the basis of a number of factors. *See* "Platinum *vs.* vanadium pentoxide as catalysts for sulfuric acid manufacture," A. Paul Thompson, *Trans. Am. Inst. Chem. Eng.*, 27, 264–309 (1931).

can be recovered from the spent mass, while the vanadium mass offers no recovery value; its main "cost" is for the license from the patent owners.

A comparison of high platinum and low platinum masses is given at the head of the chapter.

The new platinized silica gel is prepared by applying a dilute ammonium chloroplatinate solution ($[NH_4]_2PtCl_6$) to the silica gel, choosing the amount of solution such that the gel will contain 0.1 per cent Pt. Silica gel has the appearance of very coarse sand, and is as hard; it takes up 50 per cent of its weight of solution. The granules are dried, and reduced in hydrogen gas, so that the metal is liberated.

The bugbear of the early contact operators was the poisoning of the platinum mass. There are two kinds of poisoning: temporary poisoning due to chlorine, which relieves itself as halogen-free gas sweeps through the converters, and permanent poisoning, due to arsenic. In the early days of the contact process, operators were surprised that burner gas from pyrite ore, fed to the new system, gave rise to difficulties, while in the chambers they functioned smoothly; the equipment for purification from chlorine and arsenic was soon evolved, and the matter of poisoning became a matter of faulty operation. Arsenic as arsine AsH_3 was avoided by not using iron for the coolers, so that condensed acid could no longer react with iron and form the hydrogen necessary for the formation of the gas. Lead is used instead. Nevertheless, if the danger still exists, the new platinized silica gel should be selected, for it is immune to arsenic poisoning. It is generally accepted that it will operate with the same high conversion on 10 or 10.5 per cent gas from brimstone as on 8 per cent gas. It is more flexible, therefore, and takes a temporary overload without loss of efficiency, being in that respect superior to the vanadium pentoxide masses. Platinized silica gel is said to have a lower kindling temperature than other contact masses, except perhaps platinized asbestos; that is, it has a lower temperature at which it catalyzes the reaction effectively.

PURIFICATION OF GAS FROM PYRITE ORE

Although at the present time 66 per cent of the total sulfuric acid is made from sulfur, there are still important installations in which iron pyrite, and especially pyrite fines, are the source of the sulfur gas. The purification of such gas must be performed with greater care and carried further, in order to use the gas in any contact system. How long the lavish use of elemental sulfur can continue is a serious consideration, for the resources of mineral sulfur are distinctly limited.[7] A return to the more general use of iron pyrite is probable within the next 10 years. This consideration lends additional importance to the purification equipment.

The gas from a Herreshoff rotary shelf burner for fines (Part I of this chapter) or from flash combustion is rid of its iron oxide cloud in dust

[7] "Economic position of sulfur," A. M. Taylor, *Ind. Eng. Chem.*, **24**, 1116 (1932).

chambers, or dust collectors, with or without a "hot Cottrell" precipitator following, all working on the hot gas. The gas next passes through short lead towers, meeting a flow of sulfuric acid, which cools the gas somewhat and removes the arsenic in the form of oxide; this tower, it may be noted, imitates the Glover tower. After this, the gas is cooled in water-cooled 8-inch lead pipes, to room temperature; it then enters coke-packed lead boxes, a wet box followed by a dry one, to remove chlorine, and then to a drying tower with 96 per cent acid as the drying medium. (See Fig. 15.) The gas is then ready for the converters; it may be preheated within the converter, as indicated in the Chemico construction, or by outside multi-tubular heat exchangers.

Alternate arrangements provide for water washing in a tower just beyond the "hot or dust Cottrell," and this tower is followed by a second Cottrell, called the "moisture Cottrell."

The melting points for sulfuric acid of various strengths and for the oleums are extremely irregular; they are shown in Figure 16 by means of a graph. The specific gravity of the acids increases gradually to
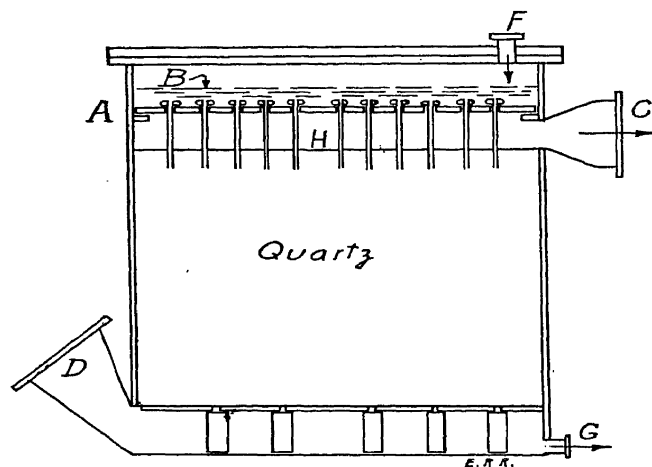

FIGURE 15.—The drying tower; A, circular plate bearing the porcelain tubes; B, level of the acid in the acid chamber; C, outlet for gas; D, inlet for the gas; F, inlet for the acid; G, outlet for the acid; H, upper level of the quartz packing.

1.8415 for the 97.70 per cent H_2SO_4, which is a maximum; it then decreases slightly to the 100 per cent acid. As a result, the specific gravity as a measure of strength over that range (96 to 100 per cent) might lead to gross errors; for that reason, conductivities are used instead.

The oleums also have a maximum specific gravity, more pronounced at 45° C. (113° F.) than at 15° C. (59° F.), as indicated in the figure.

YIELDS

A conversion of 97 per cent of sulfur dioxide to the trioxide is good practice. The unconverted gas is lost to the atmosphere on issuing from the last absorber. When sulfur as brimstone is the starting material,

additional losses are only those due to the impurities in the brimstone, which remain in the melting tank, and generally are below 1 per cent on the weight of brimstone. The over-all yield may be about 95 or 96 per cent.
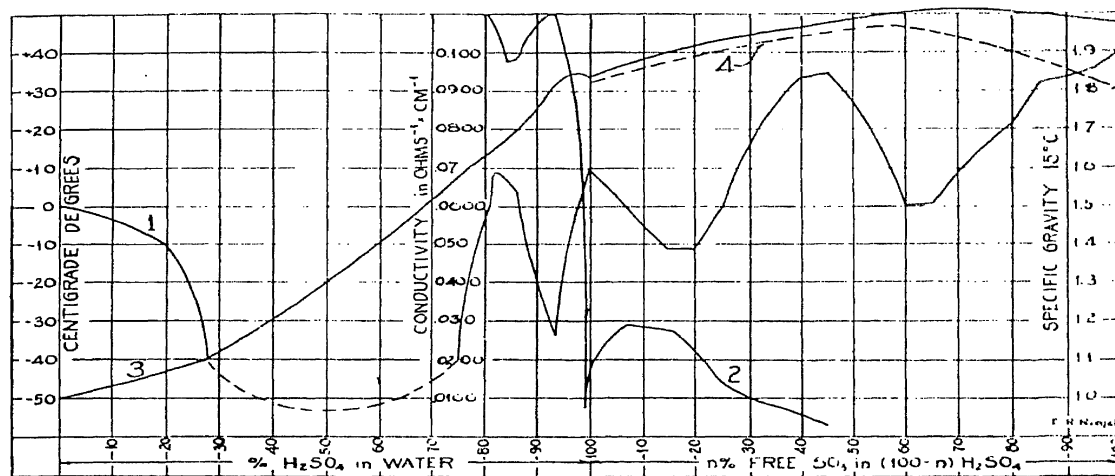

FIGURE 16.—Physical properties of sulfuric acids and oleums of various concentrations. 1, melting points (Knietsch); 2, conductivities in reciprocal ohms (Landolt-Börnstein Tabellen); 3, specific gravities at 15° C.; 4, at 45° C. (Knietsch).

When iron pyrite is used, as fines, there is a loss of about 2 per cent sulfur to the cinders. Losses occur in the scrubbing towers, coke boxes, electrical precipitators, and to a slight extent in the drying tower, so that an over-all yield of 90 to 92 per cent would be fair.

The cost of raw materials has been mentioned in the first half of this chapter. The selling price for oleums is higher than for 66° Bé. acid, which in turn is higher than for the weaker acids; the price is roughly proportional to the sulfur trioxide content, except for the strong oleums, which are considerably higher. For example: 50° Bé. acid, $8.00 a ton; 60° Bé., $10.50; 66° Bé., $15.00; 20 per cent free SO_3 oleum, $18.50; 40 per cent oleum, $42.00, all for tank car lots. The average price of 66° Bé. for 1936 was $15.50. Acids of 66° Bé. and higher strengths are stored and shipped in steel tanks, weaker acids generally in lead-lined tanks. Smaller lots are shipped in glass carboys. Acid from 61° to 65° Bé. may be shipped in steel tanks if the acid contains an inhibitor (against corrosion).[8]

THE RÔLE OF SULFURIC ACID

The uses of sulfuric acid are as varied as chemical technology; it is among the acids what lime is among the alkaline agents. If it is required

[8] Regulation of the Bureau of Explosives, Interstate Commerce Commission. Inhibitors are organic substances, such as sulfonated slaughter house waste, used in small quantities. "Practical application of inhibitors in pickling operations," F. N. Speller and E. L. Chappell, *Chem. Met. Eng.*, **34**, 421 (1927). See also "reading references."

to merely provide an acid state, sulfuric acid is chosen, provided it is not unsuitable for special reasons. Many of its numerous applications are given in subsequent chapters. Its estimated distribution is shown in Table 4.

TABLE 4.—*Estimated Distribution of Sulfuric Acid Consumed in the United States, in Short Tons of 50° Bé. Acid.* *

	1936	1935
Fertilizer	1,970,000	1,730,000
Petroleum refining	1,100,000	980,000
Chemicals	985,000	940,000
Coal products	770,000	625,000
Iron and steel	700,000	630,000
Other metallurgical uses	600,000	520,000
Paints and pigments	450,000	400,000
Rayon and cellulose film	337,000	309,000
Explosives	220,000	175,000
Textiles	108,000	90,000
Miscellaneous	380,000	326,000
	7,620,000	6,725,000

* *Chem. Met. Eng.*, **44**, 78 (1937).

The weak acid from the chambers has remained important because a dilute acid is required in the manufacture of superphosphate of calcium, a fertilizer. The standard chamber plant has the advantage of having no license fees to pay, while the newer processes of necessity involve such payments which the acid produced must carry.

For many purposes, nitrations and sulfonations of organic substances, a strong acid is required, such as 98 per cent H_2SO_4 or an oleum; the contact process must furnish these. Furthermore, an oleum may be used to bring a weak spent acid to the reaction strength, so that here also, the product from the contact plants offers an advantage; it may be said in fact that contact acid will do everything which the chamber acid does, while the converse is not true. Finally, contact acid is very pure, and is selected for certain uses on that ground.

One important use of sulfuric acid is passing; it is no longer indispensable for making nitric acid, now that the catalytic oxidation of ammonia has been perfected.

Sulfuric acid occupies its important position because the raw materials are cheap, the methods of manufacture are highly developed, and no fuel is required, except for a small amount of power. When adjunct to smelters, the raw material, the sulfur dioxide, may be said to cost nothing at all. The degree of perfection reached in both chamber and contact processes is remarkably high. The plants are practically automatic. Hand labor is needed to charge the sulfur to the melting tank; for the burners for fines, an operator must bring the ore to the top of the burners, by means of an electric truck. From that point on, the process runs by itself. As to supervision, one chamber man can watch and regulate three sets; in the contact process, one operator takes care of one or several units, by reading pressure gages, thermometers, thermo-

couples, by making chemical or thermal analyses on the sulfur dioxide gas and exit gas, and by hydrometers and conductivity readings. Some of these means of control are automatic or automatically recording, simplifying the supervision still further. A small force of laborers is required for clean-out gangs, and skilled labor for repair gangs. Labor-saving devices and automatic continuous operation distinguish the sulfuric acid industry even in an age which is characterized by them.

OTHER PATENTS

U. S. Patents: 1,660,511, on the automatic heat exchange converter for contact process; 1,675,308, on the micro-porosity of vanadium mass structure, with 23 examples of preparation formulas; 1,675,309, vanadium pentoxide masses on quartz as carrier, with several examples; 1,694,123, also on vanadium pentoxide masses with porous structures; 1,657,754, on vanadates and tungstate for the catalyst mass, with 20 examples; 1,657,753 and -4, 1,695,285, 1,696,546. 1,701,075, all on vanadium masses; 1,741,310, on stabilizers in vanadium masses; 1,518,043, on vanadium mass to be preceded by some platinum; 1,450,661, on construction of converter, as also 1,685,672, 1,660,511, 1,857,308; 1,862,746, on drying tower construction and operation (*see also* 1,384,566, 1,824,896); 1,912,832, manufacture of sulfuric acid by means of nitrogen compounds, to Andrew M. Fairlie; 1,995,292, manufacture of sulfuric acid; 2,028,739, sulfur dioxide from Spanish pyrite, removing fluorine by silica, and otherwise purifying the gas; 2,008,761 and 1,970,923, process and apparatus for producing sulfur trioxide; 2,042,675, making sulfuric acid from a sulfur dioxide containing organic impurities; 1,995,360, 2,023,203, 2,028,416, making sulfuric acid or sulfur dioxide; 2,001,359, making concentrated sulfuric acid or oleum from sulfur dioxide regenerated from sludge in petroleum refineries, to the late Ingenuin Hechenbleikner; 1,996,764, production and purification of sulfur dioxide from similar spent acid; 2,044,960, production of sulfur dioxide and iron oxide; 2,030,885, apparatus for burning sulfur; 1,942,817, catalytic apparatus; 1,971,465, catalyst for use in the contact method of making sulfuric acid, containing thallium and vanadium; 2,030,021, method and apparatus for the production of sulfur dioxide, by roasting ore.

German Patents: 459,978, sulfuric acid made in towers by an excess of nitrous gases; 463,828, on chamber acid; 455,075, for atomizing sulfuric acid; 467,587, on making all the acid in the Glover tower; 466,578, making oleum by contact process; 516,764, on a catalytic mass containing chromium hydroxide; 517,965, on a rotating oven for concentrating sulfuric acid.

PROBLEMS

11. Let it be required that a plant producing 10 tons of 100 per cent H_2SO_4 daily be erected. The brimstone is to be shipped in by boat over the sea. How much sulfur should the contract call for, over the year, the yield being taken as stated in the text?

12. A plant manager finds that there are produced in his chamber plant 40 tons of 50° Bé. sulfuric acid every day. It would be better for his sales opportunities if that acid could be strengthened to 66° Bé. acid. Could a contact plant be erected which might take the weak acid and raise its strength to the desired one? How much sulfur would be required per day?

13. The reaction heat in the converter is 45.2 Calories for $2SO_2 + O_2 \rightleftharpoons 2SO_3$. Compute the total heat in Btu. for a plant making 40 tons of 100 per cent H_2SO_4 per day. Conversion factors will be found in the appendix. Compare the number of pounds of bituminous coal which would generate the same amount of heat. (See Chapter 12 for the fuel value of coal.)

14. Make the same comparison of heats for the amount of sulfur burnt in the plant specified in Problem 13, if the heat evolved is $S + O_2 = SO_2 + 69$ Calories, and the equivalent weight of bituminous coal.

15. An 86.3 per cent total SO_3 oleum may be said to be 105.3 per cent H_2SO_4, because it can be extended by the addition of water, at least theoretically, to give 105.3 parts of such acid. It is not done actually, because the reaction with water is violent; the dilution is by means of a weaker sulfuric acid. Given the same

oleum, find the amount of free SO_3, and of the amount of 100 per cent H_2SO_4 it contains. Method: 86.3 per cent oleum contains 16.7 per cent water, hence $16.7 \times 98 \div 18$ parts of H_2SO_4. The corresponding amount of sulfur trioxide is bound and the remainder is free.

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Until recent years, the only commercial way to make nitric acid was with the aid of the non-volatile sulfuric acid, liberating the volatile nitric acid. This acid is now made from atmospheric nitrogen, via ammonia. Its production from natural nitrates has become an unimportant branch of chemical technology. From whichever source it is obtained, nitric acid is irreplaceable in the manufacture of dye intermediates and explosives, and its importance was demonstrated during the World War. The even greater importance of nitrogen compounds for agriculture is a separate consideration.

Chapter 2

Nitric Acid, Chile Salpetre, Mixed Acid, Iodine, Hydrofluoric Acid, Aluminum Sulfate

Until eight or nine years ago, nitric acid was made by the action of sulfuric acid on Chile salpetre, the commercial sodium salt of the acid. To-day, none is made from Chilean nitrate, in the United States, nor in Germany. The standard process to-day is the catalytic oxidation of ammonia with atmospheric oxygen, presented in full in Chapter 6. There are a number of plants which continue to make nitric acid by the action of sulfuric acid on synthetic nitrate, because in that way a concentrated acid is readily obtained, and because the equipment was at hand for this distillation. A brief statement on the methods will therefore be given, taking the opportunity at the same time to present some essential data on the properties of the acid.

Chile salpetre itself has lost much of the importance it once had. Its main use is as a nitrogenous fertilizer; on the basis of tonnage, its service as a raw material for nitric acid is and was secondary. In the year June 1928-June 1929, Chile salpetre equivalent to 490,000 metric tons of nitrogen were produced; in 1929-30, 464,000 metric tons; in 1930-31, 250,000 metric tons; in 1932-33, the low point, 71,000; but since then, the amount has been rising; in 1935-36. it was 192,000 metric tons of nitrogen.* This material is found in the Terapaca and Arica district in northern Chile, where the rainfall is so scant that the soluble salts present in the soil have not been washed away. The nitrate-bearing rock lies near the surface, under 6 to 10 feet of overburden, and extends to a depth of 50 feet. The method of extraction is to load the rock, called "caliche" if rich, or "costra" if poor in nitrates, into carts which are pulled by mules to the plant, to leach out the nitrates with hot water, and to crystallize. Sodium nitrate is extremely soluble in water. During the leaching the slightly soluble sulfate is left behind with the insoluble earthy portions, but the solution obtained holds other salts such as the chloride and iodate; after crystallization, these remain in the mother liquor chiefly. The iodates are a source of iodine, as described further

* See table in chapter 6.

on. A certain amount of the chlorides remains undissolved in the strong nitrate liquor and are thus eliminated; but some crystallize with the nitrate. Chile salpetre contains about 95 per cent NaNO₃, and is bought on the basis of the nitrate content as determined by difference.[1] It always contains iodates and chlorides. The nitrate is shipped in burlap bags.

A considerable amount of Chile salpetre is used in dynamite mixtures, as such, without any treatment.

NITRIC ACID FROM SYNTHETIC SODIUM NITRATE

The reaction between sulfuric acid and sodium nitrate takes place in cast-iron retorts varying in capacity between 1500 and 5000 pounds. The nitrate is shoveled in through an opening in the front of the smaller, cylindrical retorts, or dumped into the larger, square or pot-type retorts through an opening in the top, from small trucks on rails. The sulfuric acid is run in next, and then the retort is heated gently from its own
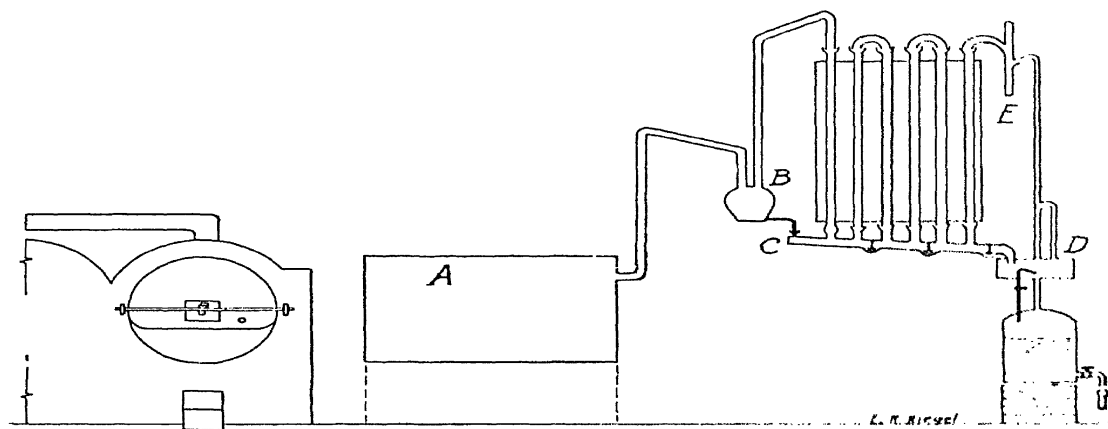
FIGURE 17.—Nitric acid from nitrates with the Gutmann condensing system. *A*, retort; *B*, collector for air-condensed acid; *C*, chamber pipe with water-cooled pipes; *D*, separator and receiver; *E*, connection to Lunge tower and chimney.

small fireplace. Nitric acid is a liquid which boils at 86° C., so that it is readily vaporized; high heat is detrimental, for it decomposes the acid. The vapors pass to a condenser cooled by water; the gases which do not condense are absorbed in water in final towers called Lunge towers. The operation of the retorts is intermittent, and for any size requires one day when working normally.

The amount of sulfuric acid is sufficient to form the acid sulfate, $NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4$; only one-half of this acid functions to liberate nitric acid, the other half remains unused. The reason for this practice is that the acid sulfate is a liquid and may be run out,

---

[1] Moisture and other impurities are determined, and the difference between their total and 100 is considered sodium nitrate.

.mount of acid in the acid sulfate, called the nitre cake, is not
per cent as the formula $NaHSO_4$ suggests, but 37, 33, even 30 per
its fusing point lies between 210° and 320° F. (99° and 160° C.).
₂ beginning of the distillation the strongest acid passes out, essen-
anhydrous; near the end, a weaker acid, as the temperature is
.. The aim of the nitric acid maker is to produce strong acid; a
n amount of weak acid is unavoidable, for on decomposing, nitric
.tself produces water; but the amount of weak acid may be con-
.bly reduced by using strong sulfuric acid 98 per cent H_2SO_4, in
:tort. The acid is brown in color, especially the concentrated acid,
o the presence of oxides of nitrogen.
₁e condensation of the vapors is done in one of two systems chiefly,
utmann system and the S-bend or Skoglund system. Other instal-
₁s are: the Hough, the Valentiner and the Uebel. The Gutmann
m is illustrated in Figure 17.

leached Nitric Acid. It is necessary, for certain uses, to produce
: acid free or almost free from the lower oxides of nitrogen (such
O, NO_2). A pale nitric acid of this type is produced by the Valen-
system which includes operation under reduced pressure (one-third
sphere); an easier way is to set up a bleacher in connection with
-bend condenser, and operating at normal pressure; this constitutes
:koglund system. The bleacher consists of a duriron (or stoneware)
r about 10 feet high and 30 inches wide, set immediately behind
etort and below the condenser. The condensed acid flows down the
r, the hot gases travel up and remove nitric oxide and dioxide from
iquid; the acid leaving the base of the bleacher is cooled by passing
₁gh a U-shaped tube set in cold water; from here it flows to the
ver. Most of the lower oxides of nitrogen reach the Lunge towers.
'he bleacher just described serves well for strong acid, such as
er cent HNO_3, which usually is to be made into "mixed acid". It is
:times desired to bleach a weaker acid, with the special purpose
₁aking it chlorine-free. This may be done by adjusting the strength
he acid to 42° Bé. at 60° F. or 15.5° C. (67.18 per cent HNO_3),
ing it in a stoneware pot set in warm water and blowing in com-
sed air filtered through glass wool. A white acid results; it is suit-
for jewelry manufacturers, who wish to recover gold from its
₁er and other alloys; it must contain no chlorine, for a chlorine con-
would cause a loss of gold. Nitric acid made by ammonia oxida-
, or from synthetic sodium nitrate, is free from chlorine.

Gas Recovery Towers. The lower oxides of nitrogen escape con-
sation when merely cooled; recovery towers are therefore provided in
ch such gases meet a trickle of water; at the same time they are
lized, at least to a considerable extent, so that the amount of nitrous
l decreases, while that of nitric acid increases. The gas usually
:ies enough air for this oxidation. The original examples designed
George Lunge have almost flat plates with perforations and ridges,
that each plate retains a certain amount of liquid which is replaced

as the liquid from above reaches it; the gas enters at the base, the water at the top. Solution of the gas takes place at each level. The strongest gas meets the rather strong solution (40 per cent HNO_3) near the base, and can enrich it somewhat; while after rising to near the top, nearly exhausted, its remaining contents are abstracted by the water, as yet uncharged with acid. This tower exemplifies the counter-current principle.

The Hough system is even more compact than the Gutmann; it is made of duriron. The Gutmann system is nearly always stoneware; the Skoglund usually has stoneware cooling pipes, which may be replaced by duriron or quartz. The Valentiner system has stoneware coils hung on a stoneware frame; these are more expensive than the simple S-bends of the Skoglund or the straight pipes of the Gutmann, so that a break is a more serious matter. The Uebel system employs three retorts working in series, and is designed for the use of weak sulfuric acid.

The specific gravities for the various strengths of nitric acid increase steadily, but more slowly, at the higher strengths, than the concentration.

|	° Bé.	Sp. Gr.	Per Cent HNO
Nitric acid (15° C/4° C)	36	1.33	52.34
"	40	1.38	61.24
"	45	1.45	77.24
"	47	1.48	86.01
"	49	1.51	98.05
"	49.63	1.52	99.62
"	49.654	1.5201	99.70

One hundred per cent nitric acid exists only as a solid at 41.3° C. (−42.3° F.); a certain amount of decomposition into the anhydride and water takes place on melting. Above 45° Bé., the acid is generally yellow to brown.

Nitric acid and water forms a constant boiling mixture with maximum boiling point, at 120.5° C. (249° F.), containing 68 per cent HNO_3. On distilling a commercial acid for purification, this is the acid which is obtained, and has therefore become the standard strength for the "C.P." acid. It is a water-white acid.

There were produced of nitric acid 100 per cent in 1935, 122,596 tons in the United States, from synthetic sodium nitrate, valued at $89 a ton, or 4.5 cents a pound.

MIXED ACID

In any nitration, as for instance in that of benzene, two products result: the nitrated body, here nitrobenzene, and water; as the reaction proceeds the water accumulates and tends to reverse the action. To prevent this, concentrated sulfuric acid is added; it binds the water, and permits the nitration to proceed to completion:

$$C_6H_6 + HNO_3 = C_6H_5 \cdot NO_2 + H_2O.$$
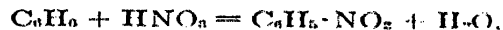
It has become customary to mix the nitric acid and sulfuric acid at the factory, before shipment to the consumer; this saves him one opera-

and the mixture may be shipped in steel car tanks, as sulfuric
is shipped, while nitric acid is usually shipped in glass. The mix-
of the two acids is called "mixed acid"; it varies in the relative
ortions of nitric and sulfuric acid it contains, and also in its water
ent, and is made up to order. Examples:

Nitration of wood pulp for "fibre"	45.0% HNO_3;	48.0% H_2SO_4
Nitration of benzene	30.0	54.0
For nitroglycerin	35.6	58.0

n order to make mixed acid, the nitric acid is elevated by means of
oneware elevator with stoneware ball valves to an upper level, and
i there fed by gravity to the mixing vessel, at about the same rate
he sulfuric acid. The mixing vessel may be a cylindrical steel tub
. paddle. Heat is evolved, which is dissipated during the slow mix-
and on standing over night. In the newer plants, the mixing room
laced at a lower level than the nitric building, so that the nitric
may be fed by gravity. The mixing is made more rapid by cir-
.ting the acid from a steel storage tank through a condenser cooled
water, and feeding the nitric acid gradually into the tank containing
charge of sulfuric acid. The circulating pump is a small steel cen-
igal pump; it draws the acid from the bottom of the tank and
vers it at the top on the opposite side. The same storage tank serves
in acid egg for loading the railway car tank, which it equals in size.
Mixed acid is almost colorless.
The production of mixed acid in 1935 was 46,074 tons, valued at
.50 a ton.

IODINE

Until 1931, the world production of iodine was about 2 million pounds
ear, and nearly all of it was made from the mother liquor of Chilean
rate; the price was $4, then $3 a pound. Since that date, the pros-
t of the complete closing down of the Chilean fields has caused a
rch for other sources of iodine;[2] this has been successful, and the
nopoly of the Chilean producers has been broken. The domestic pro-
ction was 245,696 pounds, while the imports, all from Chile, were
),819 pounds and priced at $1.12 a pound. The price in 1935, in the
ited States, for domestic iodine, was $1.05 a pound; the year before,
iad been $1.23.
The possible production per year from a variety of sources other than
ilean nitrate is:

	Tons	Source
Europe	140	Seaweed
Japan	150	Seaweed
Java	80	Artesian wells
United States	500	Oil wells (brines)
Russia	240	Seaweed and oil wells
Total	1110	

[2] "Fortunes and misfortunes of iodine," by P. F. Holstein, *Chem. Met. Eng.*, **39**, 422 (1932).

The iodine is present chiefly as iodide; the average concentration in brines is low (equivalent to 0.05 gram per liter), so that efficient and well-conceived processes must be installed.[2a]

On the other hand it is estimated that if 500,000 tons of Chilean nitrates are produced, which is one-fifth of the normal sales, enough iodine for the world's consumption could be produced, at a cost of about 50 cents a pound. The method would be the one used in the past: The mother liquor from the Chile saltpetre crystallization contains 5 grams of iodine per liter in the form of calcium iodo-chromate, calcium iodate, and some sodium iodate. The free iodine is liberated by addition of sodium bisulfite solution, in the form of a solid which sinks to the bottom of the tub.[3] It is flushed into canvas bags, washed with water several times, and pressed to a cake by means of a hand press. This crude product is then distilled from cement-lined iron retorts, heated by a coal fire; stoneware pipes are fitted to each retort and in these the iodine deposits in the form of crystals containing 99 per cent or more of iodine; the moisture in the cake escapes through the loose joints in the condensing pipes. The crystals are packed in barrels holding 120 pounds, and these are wrapped in cow hides which on shrinking form an air-tight cover which prevents the loss of iodine by sublimation. The reaction is

$$2NaIO_3 + 5NaHSO_3 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2.$$
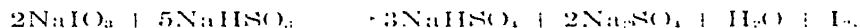
Iodine forms black, flat crystals, soluble in alcohol to a brown solution, the tincture of iodine, used in the pharmacy. It serves also for the manufacture of iodoform, of aristol (di-thymol-di-iodide) its improved substitute, and of sodium and potassium iodide. It is used by the chemical analyst, in chemical laboratories in general, and for the manufacture of a few dyes.

HYDROFLUORIC ACID

Hydrogen fluoride HF (or more correctly, H_2F_2) is a gas which is extremely soluble in water; this water solution is termed hydrofluoric acid. Hydrogen fluoride is made by the action of sulfuric acid on calcium fluoride (CaF_2) which occurs as the mineral fluorspar in Illinois and Kentucky in the United States, and in England and other countries. The original method consisted of batch distillations from small two-piece lead retorts; this has been displaced by continuous methods, of which the following is an example.[4]

A cast-iron retort 12 feet long and 3 feet in diameter is rotated at a slow rate and heated from the outside by fire gases. At the charging end A (Fig. 18) a mixture of powdered fluorspar and sulfuric acid of various strengths is fed in through a stationary disk, fitting by means of a sleeve into the rotating cylinder. A slight inclination causes the mass to move forward until it finally reaches the discharging end B.

[2a] U. S. Patent 1,944,423; 2,009,056.
[3] "The production of iodine in Chile," John B. Faust, *Ind. Eng. Chem.*, 18, 808 (1926).
[4] German Patent 262,505 (1913), to H. B. Bishop, of Brooklyn, N. Y.

: gas and moisture pass out through the opening in the stationary disk are condensed in a lead coil. The temperature at the charging end 20° C., at the discharging end 320° C.

The gas passes down a lead coil laid in water, into a receiver which a charge of water and is surmounted by a small lead tower contain-wetted lead trays. The amount of water is regulated to produce the ired strength.
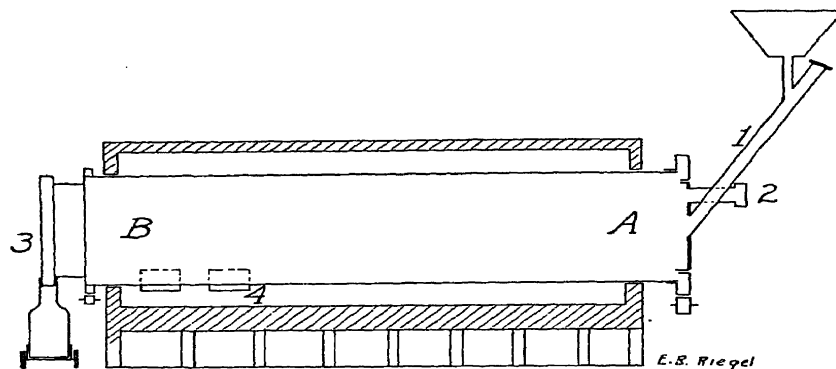

FIGURE 18.—Retort for the continuous generation of hydro-fluoric acid; 1, charging pipe; 2, outlet for gas; 3, discharge ring for calcium sulfate; 4, outlet of fire gases to the flue. The retort rotates; 1 and 2 are part of the stationary disk.

The operation is not quite continuous, for the charging must be done frequent intervals (30 minutes); the reason is that the mixed fluorspar d acid tend to set to a hard mass which gives off fumes of hydrogen oride after a few minutes. The practice is to mix the acid and mineral small batches for 30 seconds, and introduce all of it into the retort fore it can set; the evolution of the gas in the retort is fairly even. e roasted solid collects in the front end and is discharged periodically. e cylinder rotates about once in 20 seconds.

Another continuous method is that of the Rhenania Company,[5] in hich sulfuric acid, as oleum, is absorbed in anhydrous calcium sulfate; ith one-half its weight of acid the calcium sulfate is still a solid. This mixed with finely pulverized calcium fluoride, and the resulting mixed y charge may be fed to a muffle with mechanical plows, such as the [annheim furnace;[6] hydrogen fluoride is evolved as a gas and dissolved i water, using lead or platinum vessels, while the roasted solid is dis-arged continuously and, in part, used over again. In still another roposal,[7] a great excess of nitre cake replaces the sulfuric acid.

The reaction in the case of 99 per cent H_2SO_4, as the Bishop patent ecommends, is $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$. Any moisture passing

[5] German Patent 355,524.
[5] Chapter 3.
[7] German Patent 306,567.

over with the gas condenses in the cooling coil and remains in the acid solution. The usual commercial strengths are 30 per cent and 60 per cent HF; the 30 per cent acid is shipped in tight oak barrels paraffin-lined; the 60 per cent acid in rectangular lead carboys 8 in. by 12 in. by 18 in., protected by a wooden box. A certain amount of the crude acid is redistilled from lead stills and shipped in ceresin wax[8] containers containing 1 pound or less. The pure acid is colorless; its action on the skin is extremely painful and lasts many hours.

The chief uses of hydrofluoric acid are for making fluorides, for cleaning stone, and for etching glass. Mixed with sulfuric acid it serves to remove the dull surface left by the grinding tool in cutting "decorated" glassware. The fluoride of sodium is made by neutralizing the acid by soda ash. Ammonium fluoride may be made similarly, or directly by heating together ammonium sulfate and calcium fluoride, when ammonium fluoride sublimes and collects on the cooled cover of the retort.[9]

. In 1935, 2,972,161 pounds of hydrofluoric acid as 100 per cent HF were produced, valued at 15.72 cents a pound.

Fluosilicic acid may be made by the action of hydrofluoric acid on silica: $6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$; on the large scale, it is a by-product of calcium superphosphate manufacture,[10] in which the sulfuric acid with the fluoride impurity in the phosphate gives hydrofluoric acid gas, which reacts in part with the silica impurity giving silicon fluoride, SiF_4, and the two escaping together are dissolved as a weak solution (10° Bé.) of fluosilicic acid. This may be concentrated to 13 per cent H_2SiF_6, beyond which strength decomposition occurs, with loss of SiF_4. By adding soda ash, the sodium fluosilicate is made and may be concentrated to dryness; by adding magnesium hydroxide or carbonate, magnesium fluosilicate, $MgSiF_6$, of great importance to the cement industry, is obtained. Fluosilicic acid and its salts are insecticides.

In 1931, the production (U. S.) of fluosilicic acid was 3,734,000 pounds, and the price under 2 cents a pound.

Calcium fluoride may be made directly into silicon fluoride by heating it with silica in a rotating oven in the presence of magnesium sulfate; the silicon fluoride may be absorbed in a salt (NaCl) solution with the formation of sodium fluosilicate.[11]

Hydrofluoric acid is injurious to workmen; great care must be exercised in using it; rubber gloves and good ventilation must be provided.

ALUMINUM SULFATE

Aluminum sulfate is an important heavy chemical; it is used in paper making, in the textile industry, as a mordant for certain dyes, in the purification of river water for municipalities, and for a number of other purposes. The production (U. S.) of aluminum sulfate (filter

[8] Chapter 24.
[9] German Patent 94,849.
[10] Chapter 7.
[11] German Patent 319,559.

um) was: 1929, 344,962 tons; 1931, 304,767 tons; 1934, 316,759 tons;)35, 363,985 tons. In 1935, the price for "filter alum," the cheapest ·ade of aluminum sulfate, was $20.50 a ton.

Aluminum sulfate is made by dissolving finely powdered bauxite, naturally occuring hydrated alumina $(Al_2O_3 \cdot xH_2O)$, from southern rance, or from Arkansas, Georgia, Tennessee, and Alabama, in sulfuric :id of about 50° Bé. (62 per cent H_2SO_4) to which washings from :evious batches have been added.

$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O.$$
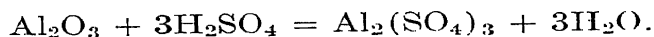
Several bauxite analyses follow:

	Al_2O_3	SiO_2	Fe_2O_3	Ignition Loss
Red bauxite (French)	58-60%	3-3.5%	1-20%	20-25%
White bauxite	50-72	6-23	1-9	20-22
Gray bauxite	56-61	7-15	1-14	21-25

Bauxite contains titanium, from a trace to 4 per cent TiO_2; it may also contain ·lenium.

'he dissolver is lead-lined, and is provided with steam coils and a cast-:ad propeller. The strong solution obtained is run to a larger tank and iluted with water sufficiently to give good settling of the undissolved iatter. After settling, the clear solution is decanted, or filtered in ·ooden frame-and-plate presses; the bottom mud or press cake is washed ·ith water, and the washings used in the next batch. In this diluting ank also, before running off the clear liquor, the iron salts are reduced y sodium sulfide, sodium bisulfite, or sulfur dioxide gas, from the brown-olored salts to the nearly colorless ferrous salts; they are not removed ·ut remain in the alum cake as ferrous salts.

The clear solution, with its iron reduced, is concentrated in a boiler intil its content of alumina is 16 per cent Al_2O_3 [12]; the solution is then un out into flat floor pans (steel) and let stand over night. In the norning the pan content is solidified to a white cake, with no sign of ·rystallization; the cake is broken by bar and chisel, reduced in a ham-ner mill [13] followed by a cage disintegrator [13] to a coarse powder, and)arreled. The floor pans are usually 20 feet by 38 feet by 4 inches deep. :n the newer plants, the pans are made a little smaller and set on a iinge so that they may be tipped when ready to dump; a hammer strikes ı blow on the under side of the pan automatically when it reaches the)roper dumping angle. The fractured cake drops off by gravity.

The preliminary treatment of the bauxite rock consists of crushing .n a swing hammer mill,[13] followed by pulverization in a Raymond suc-:ion mill.[13]

Sodic Aluminum Sulfate. One method for making sodic aluminum sulfate $Na_2SO_4 \cdot Al_2(SO_4)_3$, is to add nitre cake to aluminum sulfate solu-tion, purifying from lead and arsenic (by H_2S), and concentrating in

[12] Crystallized aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, contains 17.35% Al_2O_3.
[13] Chapter 44.

lead pans; as long as the liquor is 32° Bé., not weaker, the lead from the pan is not dissolved. Concentration proceeds, until the cooled mass gives a hard cake, which is crushed. All of the water and most of the acid are removed in a rotary roaster, yielding a mass made up of particles the size of peas. This material is milled in a Raymond mill, and forms a very fluffy white powder, used in baking powders. On dissolving in water, it must give an acid action with bicarbonate.

Potassium alum $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ is made by adding potassium sulfate solution to aluminum sulfate solution, concentrating, and letting cool and harden in crystallizers with removable sides; a small amount of mother liquor flows off the crystals, which are otherwise ready for shipment.

The production of sodic aluminum sulfate in 1935 was 18,359 tons, at $55.50 a ton.

All aluminum salts together for the United States, produced and shipped, came to 408,756 tons, worth $10,527,869 (1935).

PROBLEMS

1. It is required to produce every working day 18,000 pounds of 98.05 per cent nitric acid, from sodium nitrate containing 98 per cent $NaNO_3$; the yield to be 90 per cent. How much sodium nitrate will be required per day, at least theoretically? This charge must be divided evenly between 10 retorts, each receiving one charge per day.

2. In problem 1, how many pounds of 66° Bé. sulfuric acid (93.19 per cent H_2SO_4) will be required for changing all the nitrate into nitric acid? To make certain that no unwanted water will come from the sulfuric acid, it is later decided to use 98 per cent acid; in that case, how many pounds will be required?

3. Due to the decomposition of part of the nitric acid, water is formed, and only part of the yield is in the form of the desired strong acid. If for problem 1, 70 per cent of the recovered acid is in the form of 98.05 per cent HNO_3, the remainder in the form of weaker acid which must be marketed separately, how much nitrate and acid will have to be used?

4. The specific gravity of the 66° Bé. sulfuric acid in Problem 2 is 1.835; the amount required is measured in an elevated lead-lined box, one box for each retort, of which there are 10. The box is 2.5 feet × 2.5 feet, and 54 inches deep. To what height in the box (dipped with a lead stick) must the box be filled to provide the necessary amount of sulfuric acid? Weigh tanks are now being used rather than dip tanks.

5. In Problem 4, what is the weight of nitre cake furnished by the 10 retorts per day? The nitre cake will contain all sulfate radical introduced by the acid, all the sodium radical brought by the nitrate, and such water as the sulfuric acid brought. The sodium nitrate should be considered anhydrous.

6. The sales department calls for 2,750 pounds of 60 per cent hydrofluoric acid per day. How many pounds of calcium fluoride must be taken, if the yield is 92 per cent, and if the calcium fluoride rock contains 90 per cent CaF_2?

- 7. In Problem 6, how many pounds of 66° Bé. sulfuric acid will be required?

8. The mother liquor from a Chile saltpetre crystallization is to be worked up for iodine. It contains 9.5 grams of calcium iodate per liter, and there are 28,315 liters available. How many pounds of iodine will be obtained, the yield being 89 per cent?

9. A manufacturer converts 1,000 tons of bauxite every year, containing 58 per cent alumina of which 56 per cent enter the final product, into aluminum sulfate containing "16 per cent Al_2O_3." On the alumina in the bauxite which is consumed, the yield may be considered 100 per cent. How many tons per year does he produce? How many tons for each day of a 300-day year?

10. A mixed acid is to contain 46.0 per cent HNO_3 and 46.6 per cent H_2SO_4. There is available a 49.5° Bé. nitric acid, containing 92.03 per cent HNO_3. What

th sulfuric acid will be selected, and how many pounds by weight of each
e required to make 10 tons of the mixed acid? There are shipped every week
ank cars of this mixed acid, weighing 100,000 pounds net each. How much
acid of the strength indicated will be required over the week, and for six
ng days, how many must be produced every day?

OTHER PATENTS

S. Patents: 1,998,106, nitric acid manufacture; 2,018,397, anhydrous hydrogen
de; 2,055,283; sodium aluminum sulfate, improved method of manufacture;
423, recovery of iodine from the adsorbing charcoal; 1,998,014, iodine recov-
from impure silver iodide; 2,009,956, iodine extracted from natural brines.

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In the course of manufacture of soda ash by the old Leblanc process there was discharged into the atmosphere a steady stream of hydrogen chloride; on moist days, the neighborhood of such a plant was shrouded in a fog. Laws were passed, such as the Alkali Act in England (1863) which forbade the discharge of such concentrated gases.* It became necessary for manufacturers to erect absorbing towers, in which the gas was absorbed in water. The solution so obtained was the first commercial hydrochloric acid, then called muriatic acid, and became an important "heavy chemical." Hydrochloric acid is the first example of a waste product which has been saved and changed into a useful one.

Chapter 3

Salt, Soda Ash, Salt Cake, Hydrochloric Acid, Glauber Salt, Sodium Silicate, Bromine

Salt ($NaCl$) occurs in nature in almost unlimited quantities. It is the direct source of such sodium compounds as soda ash, caustic soda, sodium sulfate or salt cake, crystallized sodium sulfate or Glauber salt; indirectly, through soda ash, it furnishes the sodium for sodium phosphate and many other salts. Moreover it is the source of chlorine and of hydrochloric acid. It is the uses above which come to the chemist's mind when he thinks of salt; but even without these it has an imposing list of uses, which place it among the important substances in the economic world. It serves to preserve meat, fish, and hides; it is a condiment and as such appears on every table; it is used in dairies; to give temperatures below the ice point; and it is used to thaw out switches in the wintertime. Salt enables the soap maker to separate the soap from the glycerin lye, and the dye manufacturer to precipitate his products; in addition, salt is one of the important water softening agents.

The form of salt used in nearly all the chemical industries,[1] in the northern part of the United States at any rate, is rock salt, cut from the solid salt deposit by means of a shaft. There are only a few shaft mines; the three best known are at Retsof, and at Halite nearby, both in Livingston County, New York; and near Detroit, Michigan. These shafts are 1017, 1150, and 1050 feet deep, respectively. Besides these there is a shaft mine in Kansas, and two in Louisiana. The salt rock is lifted to the mouth of the shaft, crushed and screened to size, without any other operation for purification. The color is a light reddish-brown, and it is essentially pure (98.5 per cent $NaCl$). At Avery Island, Louisiana, the salt dome reaches the surface, and rock salt is mined as in shaft mines. The quality usually runs 99.4 per cent $NaCl$. The production of rock salt by states is given in Table 5. In 1935, New

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* Another Act, in 1874, prescribed that the discharge gas must not contain more than 0.0048 n of HCl per cubic foot.

[1] Except soda ash, for which the brine is better adapted.

61

York, Louisiana, Kansas and Michigan together produced 93 per cent of the total rock salt mined.

TABLE 5.—*Production of Rock Salt by States in 1931.*
(Bureau of Mines, "Mineral Resources of the United States," 1931, part II.)

	Tons		Tons
Michigan	787,040	California	310,360
New York	350,440	West Virginia	35,480
Ohio	319,450	Undistributed	130,290

* Since 1931, rock salt produced is no longer listed by states.

Salt is obtained more frequently by means of water, sent down one pipe, and after becoming saturated, brought up by another pipe concentric with the first (partly by hydrostatic pressure), and then pumped to a refining plant. Such artificial brines permit a cheaper operating cost, and are well adapted to soda ash manufacture and particularly to the making of white table salt. Artificial brines are obtained in New York State at Watkins, Ithaca, Silver Springs, Warsaw, and near Syracuse. Artificial brines are made in Michigan, where natural brines also occur but are of less importance; one field is near Detroit (Wyandotte) and a second one in the center of the State, near Midland. Kansas has many artificial brine wells; West Virginia uses chiefly natural brines; Ohio, both. In tonnage produced Michigan is first, then, in order, New York, Ohio, Kansas, Louisiana and California.

In the dry climate of the western States, salt is found as an outcrop at the surface [2]; in some of these States such salt is utilized to some extent.

In southern California, as also in Spain and southern France, the sea water is concentrated in wide basins, by solar evaporation, until the salt deposits; by running off the mother liquors at that point, the bitter magnesium salts are removed. An interesting application of the same method is at Salt Lake, Utah. Of the many salt deposits of the world, those at Stassfurt, Germany, underlying the potassium salt beds, deserve mention because they are several thousand feet thick. The bed at Retsof is 8 feet thick; the stoutest bed in America is one in Kansas, 400 feet thick,[3] while a Texas salt dome is said to be 3000 feet thick.

From the brines, whether artificial or natural, a grade of salt suitable for table and dairy use is made by solar evaporation (in the sunny climates), by open pan evaporation, or by evaporation in vacuum pans, with one pan (single effect) or several pans (double or triple effect); in the latter the steam raised from the salt solution in one pan becomes the heating steam in the next pan.[4] The evaporation of salt solutions offers this difficulty, that salt is about as soluble in cold as in hot water, so that cooling a hot strong solution is not enough to form crystals; the

[2] From the streets of the town of Salina, Sevier County, Utah, outcrops of salt may be seen at the side of the hills; its color is red, and it may be fed to cattle.
[3] "Technology of salt making in the United States," W. C. Phalen, *Dept. Interior Bull.* No. 146, 1917, p. 124.
[4] Chapter 43.

water must actually be removed from the hot solution, until the salt drops out for lack of solvent.

The precipitated salt is dried in rotary driers, frequently constructed of monel metal.

TABLE 6.—United States Salt Production in Short Tons.*

| | 1935 | | | 1934 | | |
		Price	Per Cent of Total		Price	Per Cent of Total
Salt from all sources..	7,926,897	$2.66	..	7,612,074	$3.00	..
Evaporated salt	2,330,042	6.20	29	2,281,453	6.48	30
Salt used in brine form	3,837,613	...	49	3,417,439	...	45
Rock salt	1,759,242	2.89	22	1,913,182	3.30	25

* Bureau of Mines

There were 74 plants in operation in 1935, 73 in 1934; the production of salt in all forms is comparatively steady, as may be seen by comparing the figure for 1931, 7,358,070 tons, with those given in the adjoined table. The 1931 figure was 14 per cent below the record production of 1929.

SODA ASH, THE COMMERCIAL SODIUM CARBONATE

In the United States, soda ash from salt is made by the ammonia process exclusively; in England, a certain amount, decreasing yearly, is made by the older Leblanc process; but even there, over three-quarters of the total production is by the ammonia process. In France, Belgium, Germany,[5] and other countries, the soda ash made is ammonia soda. To some extent, natural soda is isolated from the accompanying salts; such natural sodas and the ashes of seashore plants were the only source until Leblanc invented his process, in the closing years of the eighteenth century.

The ammonia soda is usually called Solvay soda, for the successful manufacture, in 1864, by this process is due to Ernest Solvay, a Belgian, and many of the devices still in use were patented by him. The process is based on the fact that when ammonium bicarbonate is added to a saturated solution of common salt, the ammonium salt dissolves and sodium bicarbonate separates as a solid; if filtered, dried, and calcined, it is changed to soda ash, or sodium carbonate, Na_2CO_3:

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl$$
$$2NaHCO_3 + heat \longrightarrow Na_2CO_3 + H_2O + CO_2.$$
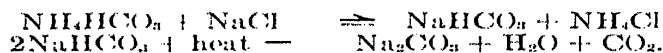
This simple principle proved difficult of application, for ammonia is comparatively expensive, and unless it is all recovered, or nearly all, the process cannot live.[6] It was the nearly complete recovery of the ammonia which enabled Solvay to defeat the well-established Leblanc soda process.

[5] The Honigmann process produces about half the ammonia soda manufactured in Germany; the other half is Solvay soda.

[6] The minimum amount of ammonia in process is one-third the amount of soda ash it helps make; taking the low price of 5 cents for 1 lb. NH_3, and 1½ cents for soda ash, the ammonia in process is worth as much as the material produced.

In practice, a saturated salt solution is treated with ammonia gas, and this solution is then saturated with carbon dioxide; the resulting suspension of sodium bicarbonate in an ammonium chloride solution is filtered, and the sodium bicarbonate is dried and calcined. (*See* Fig. 19.) The ammonium chloride filtrate is treated with lime and steam to recover the ammonia. The danger of losing ammonia in this operation is not great; it is rather in the gas leaving the carbonating vessels and in that leaving the calcining vessel that provision must be made to recover any ammonia which it may contain.
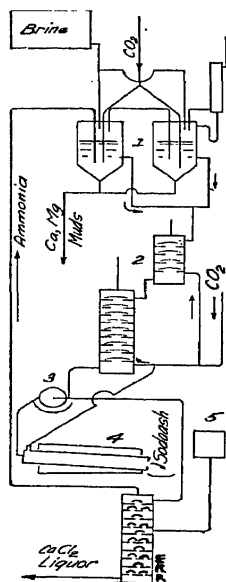
FIGURE 19.—Simplified diagrammatic flow sheet for the Solvay ammonia soda process. 1, brine tanks with ammonia absorption; 2, carbonating towers; 3, rotary suction filter; 4, calciner, producing the finished product; 5, milk of lime box for ammonia still below. The ammonia circulates. Lime kiln not shown.

The carbon dioxide is obtained by burning limestone, and this furnishes at the same time the lime necessary for treating the ammonium chloride solution. It is clear that much fuel is required to burn the limestone, to calcine the sodium bicarbonate, and to raise steam for the ammonium chloride still. For the reaction proper, no fuel is required.

The ammonia process has one imperfection, in that the chlorine which common salt furnishes is not recovered, except to a small extent; it passes to the sewer in the form of a solution of calcium chloride.

Ammoniating the Brine. As a rule, soda ash plants are located near the source of salt; thus the Syracuse, N. Y., plant formerly drew brines from the property, and now that a greater supply is needed, brine from Watkins and the neighborhood is piped to Syracuse, about 20 miles away; the brines flow by gravity. At Wyandotte, Mich., huge deposits of salt are available. The great Dombasle plant in Lorraine, France, was also located there because of the almost limitless supply of salt in

the region. Rock salt may be shipped in by rail, which, however, involves an extra expense for freight. The brine must be freed from calcium and magnesium salts, which tend to clog the carbonating towers in the later steps. This purification takes place in the same vessels in which the ammonia is absorbed. Such vessels are usually upright cylinders 15 feet high and 12 feet wide, with covers and conical bottoms. Ammonia dissolves in brine with evolution of heat, so that cooling cells hung from the cover and containing flowing cold water form part of the absorber. Towers with shelves may also be used, with cooling coils outside.

The brine run into the absorber does not fill it, for space for expansion must be left; as the ammonia gas dissolves, the volume increases. At the same time, the solubility of the salt diminishes; by feeding in dry ammonia gas, thus avoiding moisture which would dilute the brine and disturb the conditions, the desired amount of ammonia may be introduced while the salt content remains at the saturation point for that particular ammonia content.[7] A saturated salt solution at 15° C. contains 318 grams of NaCl per liter of solution, if no ammonia is present. A solution containing 60 grams of ammonia per liter is saturated with respect to salt if it contains 275 grams NaCl per liter, also at 15° C. This amount of ammonia requires only 206 grams of NaCl for the reaction, so that there is an excess of 69 grams of salt (33 per cent); because some ammonia remains as ammonium bicarbonate, since the reaction $NH_4HCO_3 + NaCl \rightleftarrows NaHCO_3 + NH_4Cl$ does not run to completion [to 73 per cent for good operating conditions], the excess salt is really somewhat greater. The excess of salt is desirable first because it drives the reaction to the right, second, because it diminishes the solubility of the sodium bicarbonate.

A certain amount of carbon dioxide gas is sent into the absorber at the same time, but not enough to form ammonium carbonate; the calcium, most of the magnesium,[8] and all the iron salts precipitate, and collect in the cone. After the proper amount of ammonia has been absorbed, the solution is settled and the clear ammonia-brine blown by compressed carbon dioxide to the carbonating tower. A loss of ammonia during the treatment of the brine is avoided by connecting the outlet pipe of the absorber to a small tower with shelves, down which a fresh brine solution travels. By using a battery of absorbers, a supply of ammoniated brine is always ready.

There are two sources of carbon dioxide; one is the limestone kiln which furnishes gas containing 35 to 40 per cent CO_2, the rest mainly nitrogen; the other source is the furnace in which the sodium bicarbonate is calcined; its gas may be as high as 95 per cent CO_2. This second portion of the gas may be considered as circulating. In some plants, the

[7] Some salt may separate out as a solid, which then passes out with the settlings.

[8] A magnesium salt content in the brine is not desired, and yet if the amount is small, and it escapes precipitation by the ammonia, which occurs because ammonia is a poor reagent for the purpose, its presence may be an advantage. Magnesia forms glass-like double salts with NaCl, which coat the walls of the apparatus, and prevent the contamination of the soda by iron with its subsequent decoloration. The factory experience is that those plants which occasionally have their soda colored red (unsalable) operate with magnesia-free brine.

two gases are combined in the pump house and no distinction is made; in others, they are used as indicated further on.

Carbonating the Ammoniated Brine. In the Solvay system, carbonation is performed in towers with shelves, on the counter-current principle; the brine flows downward, the gas enters at the base and
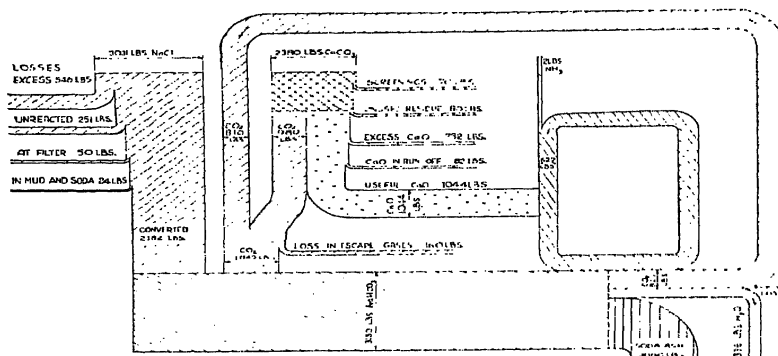

FIGURE 19a.—Diagrammatic sketch of the amounts of raw materials, circulated chemicals, products and discards in the Solvay process for soda ash. The widths of the columns and frames are in proportion to the weight of the materials they represent. (After Kirchner.)

travels upward; the other systems are gradually adopting the towers. Two towers are used in many of the plants, instead of the original single tower; a short first tower, in which enough carbon dioxide is fed into the solution to form neutral ammonium carbonate:

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3. \tag{1}$$

In the second, taller tower, enough additional carbon dioxide enters to form the bicarbonate:

$$(NH_4)_2CO_3 + H_2O + CO_2 = 2NH_4HCO_3. \tag{2}$$

In other plants, the tower is a single unit, and there are several towers. If there are five, to take an example, four would be actively precipitating bicarbonate; the fifth one would receive the ammoniated brine from the saturators, as well as a moderate flow of lean gas (40 per cent CO_2), delivering at its bottom outlet a clear liquor, carbonated as required by reaction (1). The temperature is allowed to rise, reaching 32 to 40° C., [90 to 104° F.]. The partly carbonated ammoniated brine is an active solvent for incrustations of bicarbonate, which form in spite of the engineers' skill. This procedure then has as object (1), the partial carbonation of the ammoniated brine, (2), the removal of the crusts. Each tower in turn works four days, and on the fifth, it is rid of all obstructions. From the fifth tower, the clear liquor is

divided and fed in equal amount to each one of the four working towers. The flow of brine through the fifth tower is four times faster than its flow through the working or precipitating tower.

On traveling down the working tower, the liquor meets a flow of strong carbon dioxide gas, traveling upward. Reaction (2) takes place, and simultaneously, reaction (3).

$$NH_4HCO_3 + NaCl \rightleftharpoons NaHCO_3 + NH_4Cl \qquad (3)$$
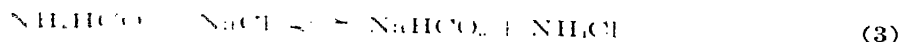
The temperature rises to 65° C. [149° F.]; by means of the cooling pipes provided in the lower sections of the tower (see sketch), the temperature may be lowered. It is essential not to lower it too far, however, for at low temperatures the sodium bicarbonate forms in such finely divided form that it cannot be filtered. The temperature of 26 to 27° C. [78.8 to 80.6° F.] has been found to be right for the production of grains of the proper size.

The tower consists of the upper 28 sections, each 15 inches high, surmounting the lower 9 sections which are 42 inches high. The material is cast iron. Each upper section has a floor with central opening, over which a dome-shaped cover is supported by three brackets. The rising gas is deflected sidewise by the domes. The lower sections have nests of cooling tubes; for the latter, wrought iron has proved a little more durable than cast iron. Other details may be obtained from figure 196. It may be well to point out that this tower is not a bubble tower; the rising gas has no liquid seal to overcome; it meets only the rain and foam of the descending liquid or slurry. Each shelf is flushed clean of deposit twelve times by the descending liquid.

A tower such as shown has a daily capacity of 50 tons of finished soda.

The brine containing 60 grams of ammonia per liter requires 83 grams carbon dioxide to form the neutral carbonate, a part of which is added in the absorbers. For the bicarbonate, an additional 83 grams must be added; in fact, a little more is required, for some carbon dioxide passes out unused from the top of the main tower. It carries away some ammonia, which is recovered with part of the carbon dioxide, in a supplementary tower fed with fresh brine.

The carbon dioxide gas enters at the base of the tower under a pressure of 30 pounds. As it rises, much of it is absorbed and the pressure drops. At the top of the tower the unabsorbed portion and the inert gas (nitrogen) pass through a supplementary tower where fresh brine removes any ammonia carried out.

The suspension is drawn off from the lowest compartment at frequent intervals, and fed to the trough of a continuous suction filter, either of the drum type or the single-disk type. The cake is washed to remove all ammonium chloride; at the same time about 10 per cent of the bicarbonate is also dissolved and lost. In spite of the washing there is left some ammonium bicarbonate in the cake, and its ammonia must be recovered; this is easily done, fortunately, for the ammonia passes out
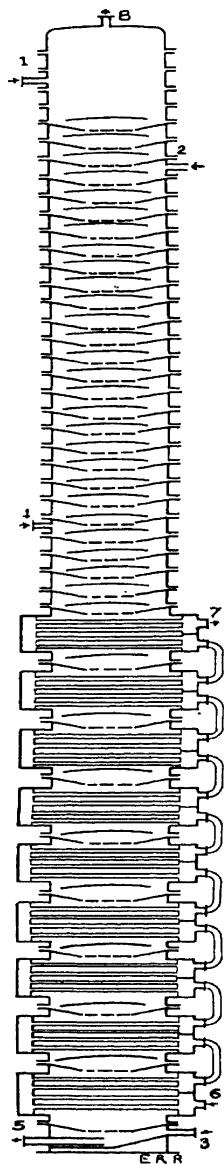
FIGURE 19b.—A carbonating tower in the ammonia soda process (Solvay); it is 69 feet high, and 6 feet in diameter.

1. Entry for ammoniated brine, used when the tower is being cleaned.

2. Entry for the ammoniated brine for the regular bicarbonate precipitation.

3 and 4. Carbon dioxide entries.

5. Outlet for the bicarbonate slurry.

6. Cooling water inlet, and

7. Its outlet.

8. Escape for uncondensed gases.

The supports for the domes not shown. (Modeled after Kirchner, p. 41.)

with the carbon dioxide on calcining the sodium bicarbonate, and the two gases together are sent to the carbonating tower.

Calcining Sodium Bicarbonate. A great variety of devices are used for the calcining of the bicarbonate, which is by no means an easy operation. In Europe a covered pan with semicircular cross-section and scrapers having a sidewise motion (Thelen pan), with outside firing, is

much used. In America, the rotary furnace with horizontal axis, with outside firing, is favored; to prevent the forming of insulating crusts on the walls, some of the hot cake just discharged is mixed with the cake to be calcined. The gas is saved in all cases, and forced into the carbonating devices.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$
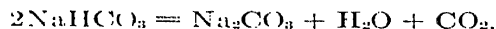
The discharged cake is light; for many uses, a denser cake is demanded; by calcining at a higher heat, the density is raised, but the dense soda ash of commerce is made by adding water to the light soda, and recalcining.

An analysis of a good commercial soda ash made by the ammonia soda process follows:

	Per Cent
Na_2CO_3	99.50
$NaCl$	0.20 to 0.25
Na_2SO_4	0.02
Insoluble	0.02
Moisture	balance

There is a tremendous sale for the bicarbonate to be used for baking powders, but for this purpose, the material must be purified, chiefly of ammonium salts. The crude sodium bicarbonate may be recrystallized, or a solution of soda ash may be carbonated. In 1935, 135,000 tons of refined bicarbonate were produced, and sold at $29 a ton.

There is also a market for crystallized sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, called sal soda, and made by cooling a solution of purified sodium carbonate of the proper concentration. In 1931, 48,480 tons were produced, with a market price of $27 a ton.

Ammonia Recovery. The bulk of the ammonia is present as ammonium chloride, NH_4Cl, in the filtrate from the bicarbonate; some ammonia is present as carbonate, carbamate, bicarbonate. The recovery is performed in a modern ammonia still, such as the one shown in Chapter 14, in which the free ammonia (carbonate, sulfide) is driven off first, and then only is there lime added in order to liberate the fixed ammonia (sulfate, chloride).

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$
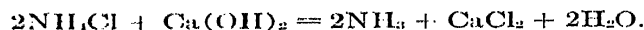
The calcium chloride passes out at the bottom of the still.

The run-off from still or tower contains no ammonia, or only a trace; it is blown by steam pressure to compartment settling tanks, and there settled; the clear liquor is removed, and the semi-solid lime mud carted to the dump.

The ammonium chloride liquor contains about one-third of the original salt (NaCl) unchanged; it is better to waste it than to have a less complete reaction. The calcium chloride formed is partly wasted; but **part of it is made into a concentrated calcium chloride liquor, the "brine" of the refrigerating plants; the diluted solution is also used to**

sprinkle on dirt roads.[9] A considerable portion of the calcium chloride formed is evaporated to dryness, and used as stated below under natural calcium chloride.

A lime kiln which allows the recovery of the carbon dioxide is used (Chapter 9). The gas from such a kiln contains the fire gases as well as the carbon dioxide from the limestone, and also dust. It is passed through a three-tray box, where it meets running water; the dust deposits, and the gas is cooled. From here it is forced into the carbonating tower.

Natural soda occuring mixed with sodium chloride and sulfate as well as magnesium salts may be isolated by treating the solution with carbon dioxide; sodium bicarbonate precipitates, is filtered off, and calcined to soda ash in horizontal rotary cylinders.[10]

The production in the United States for 1935 follows:

	Tons
Soda ash by ammonia process	2,508,559
Natural and electrolytic soda ash	94,865

The selling price in 1935 was $15.19 a ton for ammonia soda, while in 1929, it was $19.00 with a similar production. The natural soda ash, 93,230 short tons (valued at $12.80 a ton), was produced from brines from Owens Lake and Searles Lake, in California (1935).

The estimated distribution of soda ash sales is given in Table 7.

TABLE 7.—*Estimated Distribution of Soda Ash Sales in the United States (in short tons).**

Consuming industry	1935	1936
Glass	664,000	780,000
Chemicals	610,000	670,000
Soap	170,000	184,000
Cleansers and modified sodas	100,000	120,000
Pulp and paper	80,000	90,000
Textiles	48,000	44,000
Exports	43,500	44,000
Water softeners	35,000	38,000
Petroleum refining	8,000	8,000
Miscellaneous	112,500	140,000
	1,871,000	2,118,000

* *Chem. Met. Eng.*, 44, 77 (1937).

Natural Calcium Chloride. The mother liquor from the salt crystallization contains calcium chloride and magnesium chloride mainly. A good part of such liquors is concentrated to a high salt content, and then "flaked" on a flaking machine or chip machine. The product is packed in paper-lined burlap bags and serves in the treatment of roads, coal and coke for dust prevention, on tennis courts, for refrigeration, and a variety of other purposes. In 1935, 83,546 tons of this calcium-magnesium chloride were produced from natural brines in the United States.

[9] Calcium chloride is hygroscopic and retains enough moisture to lay the dust.
[10] The sesquicarbonate of sodium, often mentioned in the literature on natural soda, is $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, and is also called "trona."

SALT CAKE

Salt cake, the commercial anhydrous sodium sulfate, was produced originally by the action of sulfuric acid on salt (NaCl) in the pot and muffle process; within the last thirty years, the use of nitre cake instead of the free acid, with the sodium chloride, roasted in mechanical furnaces, rendered the first process obsolete. It was partly in order to consume the nitre cake on the market that the mechanical salt cake furnace was developed. To-day there is so little nitre cake that there is not enough for the domestic market. In 1935, 27,933 tons of nitre cake were reported produced (U.S.); in 1927, 153,615 tons. The tonnage of salt cake produced has also dropped, partly for the lack of nitre cake. This is perhaps not a real reason, however, for nitre cake may be made from salt and sulfuric acid: $NaCl + H_2SO_4 = HCl + NaHSO_4$. This nitre cake, which has never seen nitre, may be mixed with salt and fed to the mechanical furnace just as well as the true nitre cake. The amount of hydrochloric acid produced, let it be noted, is twice as great, and a market must be available for the additional amount. Less salt cake is produced when starting with sulfuric acid, than when starting with nitre cake from the old nitric acid still, for this nitre cake is already half salt cake.

The shortage of salt cake comes at a time when one of its main consumers, the sulfate process for wood pulp, has increased its requirement tenfold over its needs of twelve years ago. A large proportion of salt cake for this industry had to be imported (110,379 tons in 1935).

The still young mechanical salt cake furnace faces another difficulty. Not only is the nitre cake, which brought half the salt cake, almost off the market and no longer produced in sizable amounts, but other sources for hydrochloric acid have restricted the market for its second product. All these factors conspire to make the mechanical salt cake furnace a less important device.

THE MANNHEIM MECHANICAL SALT CAKE FURNACE

The best known mechanical furnace is the Mannheim [11] furnace. It is an automatic device, with continuous operation; the labor is a minimum; especially is the labor of pulling out the fuming salt cake by hand rakes, a suffocating operation, rendered unnecessary. When using nitre cake, the reaction is $NaCl + NaHSO_4 = HCl + Na_2SO_4$; it takes place to near completion at 650° C. (1202° F.).

The Mannheim furnace consists of a circular muffle of cast iron, 12 feet in diameter, with bottom and top dish-shaped; the inner height at the circumference is 20 inches, in the center 40 inches. A shaft penetrates it from below and carries four arms, each of which carries two cast-iron plows. The shaft is rotated slowly, 1 revolution in 2 minutes, by the gear and pinion indicated in Figure 20. The mixed salt and nitre cake is fed in from the top near the center, and is moved to the circumfer-

[11] German Patent 137,906 (1900), Mechanischer Calcinirofen, by the Mannheim Verein.

ence by the plows. Plow 8 is wider than the others, and discharges the burned cake (now salt cake) through the opening of the chute (Fig. 21). Here the cake accumulates to some extent and is removed in small trucks
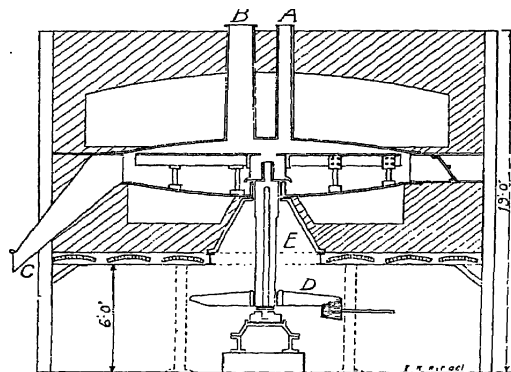

FIGURE 20. — Mannheim mechanical salt cake furnace, with hydrogen chloride as by-product. The charge enters at *A* and is discharged at *C*; the gas passes out at *B*. The eight plows are rotated from below, by gear *D*; the shaft may be water cooled at *E*

to the storage bins. The discharged cake is yellow and turns white on cooling.

Some of the details of construction of the muffle will be plain from the illustrations; the bottom is a single casting, also the top. The sides consist of a number (12) of curved castings which assembled provide three doors; one of these is over the discharge opening and chute. Each plow differs in length of shank; and each is slightly turned so that the cake is swept outward. The heat is furnished by a small fireplace. The fire
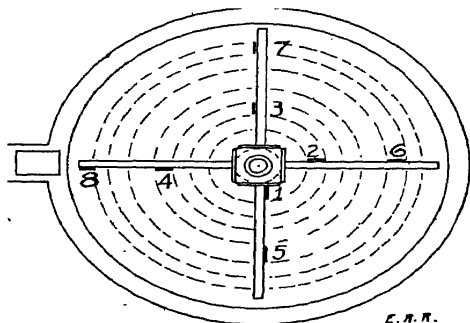
FIGURE 21.—Plan view of the Mannheim furnace, showing bottom casting, the eight plows, and the lanes which they sweep.
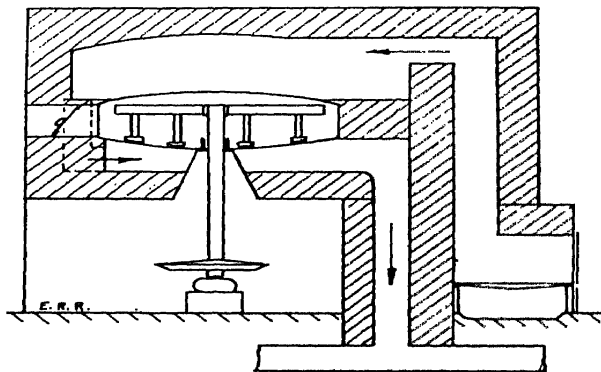
FIGURE 22.—Circulation of the fire gases around the Mannheim furnace.

gases enter over the muffle, heating the top; then travel to the under side by a passage in the brickwork and heat the lower side; from here they pass out to the chimney. (*See* Fig. 22.) The temperature is registered

by a platinum resistance pyrometer [12] placed in a protecting cast-iron tube reaching into the center of the muffle from above.

The salt used is rock salt, of the fineness of sand; it may be either purchased in that form, or if coarser, reduced in a swing hammer mill.[13] The nitre cake, in pieces 1 foot across or smaller, is fed to a pot crusher [13] or jaw crusher [13]; the product, the size of walnuts, is reduced to a coarse powder in a squirrel-cage disintegrator [13] or a swing hammer mill. Salt and nitre cake are carefully mixed in some plants by placing equivalent quantities (250 pounds of salt and 700 pounds of nitre cake, for example) in a rotating cylinder and mixing for 15 minutes. In other plants merely dumping salt and nitre cake alternately into the hopper serving the screw conveyor which brings the cake to the feed pipe of the muffle is found to give sufficient mixing.

The reaction is preceded by a fusion; the nitre cake fuses first. The effect of high sulfuric acid on the fusion point of nitre cake is not so great as that of the moisture content; 10 per cent moisture lowers the fusion point from 320° F. (160° C.) for the dry cake with 37 per cent H_2SO_4 to 210° F. (99° C.); while 10 per cent sulfuric acid added to the dry nitre cake has almost no effect on its fusion point.

Temperature and Capacity. The temperature of the muffle is indicated by the pyrometer and is not kept constant, but is increased slightly as the wearing of the plows progresses; it lies between 625° and 675° C. The guide is the daily analysis of the salt cake. A well burned salt cake should contain 2 per cent or less NaCl, 1.5 per cent or less H_2SO_4; if the cake runs higher in both impurities, the temperature may be increased. Other ways to control the quality are to change the relative proportions of salt and nitre cake, and the absolute weight fed in. In the 12-foot diameter muffle, six tons of good cake may be produced per day.

Length of Run. The plows will need renewing every two months (approximate figure); the bottom casting may last two years, but one year is considered fair enough; the top casting and the sides will outlast several bottoms. The life of the plows may be lengthened by making the blade of duriron [14] and bolting this to a cast-iron shank.

Safety Flange. Should a plow become jammed against some foreign object a break may occur in the gears, which would be an expensive accident. This is prevented by fitting the pinion shaft with two flanges working through a pin whose size is chosen just sufficient to carry the load. Any sudden resistance will break it, and at the same time indicate that the obstruction must be removed.

Pot Stills. The dwindling amount of available nitre cake from the nitric acid retorts is supplemented by the product obtained as still residue when salt is treated with sulfuric acid in the proportions indicated by the reaction: $NaCl + H_2SO_4 = NaHSO_4 + HCl$.

[12] Chapter 46.
[13] Chapter 44.
[14] Chapter 45.

The Laury Furnace. The second well-known furnace installed in American plants is a two-stage rotary cylindrical furnace,[15] not unlike the cement furnace, but shorter and stouter.

The production of salt cake (U. S.) dropped from 206,612 tons in 1929 to 121,366 tons in 1931 and rose to 169,197 tons in 1935; the portions which were sold on the open market brought $12.00 in 1929, $15.00 in 1931, and $11.00 in 1935.

The use of salt cake for making Kraft paper has been mentioned; it forms part of the batch for the window glass furnaces, is the raw material for Glauber salt, for sodium sulfide, and serves in other numerous minor rôles.

Natural sodium sulfate, produced in the United States and shipped, was 38,706 tons valued at $9.75 a ton, in 1935. The principal sources were Campe Verde, Yavapai Co., Arizona; Mina, Mineral Co., and Wabuska, Lyon Co., Nevada; Casper, Laramie Co., and Rawlins, Carbon Co., Wyoming. Almost an equivalent amount was shipped from Canadian deposits (Saskatchewan).

The Leblanc Process for Soda Ash. In the Leblanc process,[16] salt is treated with sulfuric acid, giving sodium sulfate and hydrogen chloride; this first step was retained for the manufacture of hydrochloric acid with sodium sulfate as a by-product. The salt cake (sodium sulfate) mixed with limestone and coal is heated in a short rotary furnace, producing the "black ash" which after leaching with water gives a solution of sodium carbonate containing also caustic. This solution is evaporated by the waste heat of the black ash furnace, during which process it receives enough carbon dioxide to form all carbonate. The monohydrate $Na_2CO_3 \cdot H_2O$ separates, and is dehydrated completely in reverberatory furnaces. A part of the soda ash was made into caustic soda by treating the solution with lime, so that a lime kiln usually formed a part of the plant. The Leblanc process, even though no longer practiced, is one of the most famous processes in industrial chemistry. In the course of its development, fundamental engineering principles were recognized and firmly established (the counter-current principle for example in the Shanks system of lixiviation).
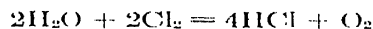
HYDROCHLORIC ACID

Hydrochloric acid is made (1) from salt, in salt cake furnaces; (2) by burning electrolytically produced chlorine in excess hydrogen; (3) as by-product from the chlorination of hydrocarbons such as pentane and benzene.

$$C_6H_6 + Cl_2 = C_6H_5Cl + HCl$$

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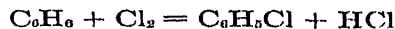
[15] U. S. Patent 1,435,930 (1922) to N. A. Laury.

[16] Invented during the period of the French revolution, by Nicholas LeBlanc, a physician. The inventor did not receive the promised prize from the government, and his plant suffered from the political upheavals. For a century, civilization has enjoyed abundance of window glass, inexpensive soap, thanks to LeBlanc's genius, but he himself died unrewarded, unthanked, in an asylum, by his own hand.

A fourth method [17] employs chlorine and steam over heated coke (350° C.; 662° F.) containing iron compounds as catalysts, or charcoal, to which iron oxide has been added.

$$2H_2O + 2Cl_2 = 4HCl + O_2$$

Hydrogen chloride is a gas; on cooling to room temperature, it does not condense to a liquid, as does nitric acid, but it must be dissolved in water. The ordinary commercial strength is 20° Bé., at 60° F. (15.5° C.), containing 32.46 per cent HCl. The system for absorption is essentially the same, whichever method for the production of hydrogen chloride is employed. As an example, the gas from a Mannheim furnace may be taken.
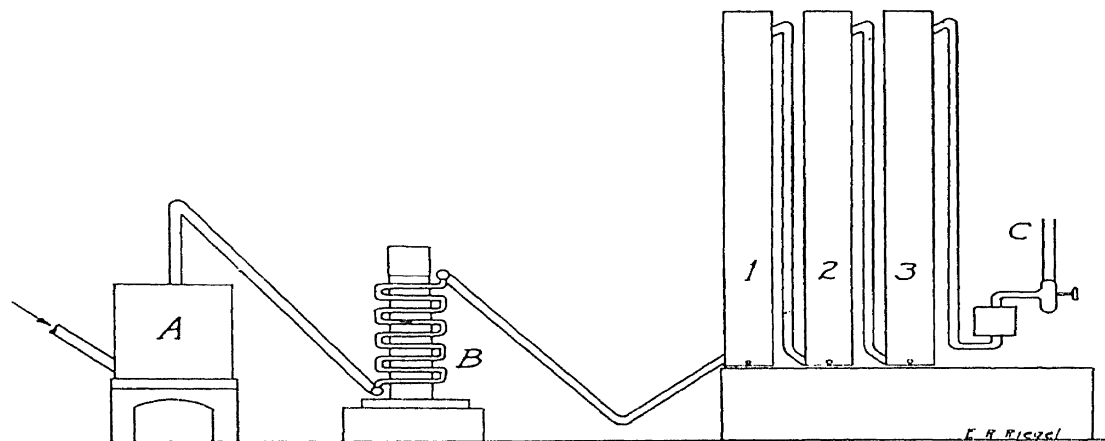
Figure 23.—Absorption system for hydrochloric acid; the gas enters dry box A, then cooler B, and the absorbing towers 1, 2, and 3; the exhausted gas passes out at C.

The gas from the Mannheim furnace passes through a 10-inch stoneware line, coated with tar to close the pores, to a short stone box, where it cools further and deposits most of the sulfuric acid which it carries. From the stone box, it passes to S-bend coolers or to Cellarius vessels set in running water; the cold gas then passes to the absorbing towers, where the solution in water or weak acid takes place. Tower No. 3 receives cold water, and delivers at the base a 12° Bé. acid, which is warm; before feeding it to No. 2, this acid passes through about 6 lengths of 1-inch glass tubing set in cold water. The cold acid is elevated to the top of No. 2 by a small automatic, hard-rubber-lined elevator, or by a "monte-jus",[18] a gentle stream of air into a 1-inch glass pipe so that it forms gullets of liquid which give a broken column easily pushed up. The acid solution from the base of No. 2 is cooled

[17] German Patent 427,539 (1926); see also "Manufacture of hydrochloric acid from chlorine," Wilhelm Hirschkind, *Ind. Eng. Chem.*, 17, 1071 (1925).
[18] *Monte-jus* is French for juice-raiser.

and fed to No. 1, where its maximum strength is obtained. The acid from No. 1 after cooling is the 20° Bé. acid ready to ship. The daily production for a furnace furnishing 6 tons of salt cake is about 9000 pounds of 20° Bé. acid.

The towers are made of stoneware, usually in 10 sections, each 30 inches high, and 36 inches in diameter; the packing is coke, of carefully selected sizes, or 3-inch spiral rings of stoneware. Three towers are sufficient for complete absorption, but in many plants four are used, and in the summer months, even five.

The gas is pulled through the absorbing system by a fan set at the exit from the third tower. (*See* Fig. 23.) The fan is protected from acid mist by a small coke box, so that a lead-lined fan or even an ordinary steel fan may be used. The suction exerted on the system is so regulated that it is felt at the muffle just enough to prevent the gas from passing
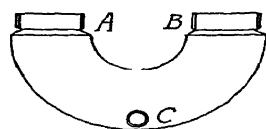
FIGURE 24.—Cellarius stoneware vessel for gas cooling; the gas enters at *A* and leaves at *B*; the vessel is set in running water, with only the bells protruding. *C* is the outlet for any liquid which may condense.
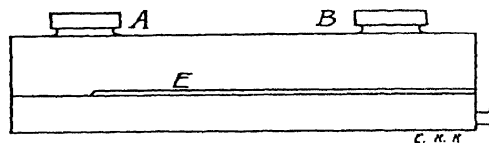
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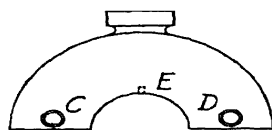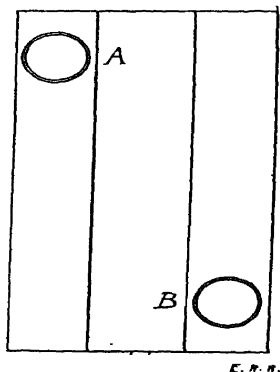
FIGURE 25.—Cellarius stoneware vessel for acid cooling and absorption; the gas enters at *A* and leaves at *B*; the acid solution enters at *C* and must travel to the rear of the vessel and then forward again in order to reach the outlet *D*, because dam *E* is in the way. The vessel is submerged in water.

around the working doors into the room. The strong gas may also be propelled by a stoneware fan set between the cooler and the first tower.

The stone box is built of sandstones which have been boiled in tar to prevent the acid from penetrating them; the stones are held together by cast-iron corner pieces and rods. The joints are made tight with rubber gaskets, or with asbestos cord smeared with china clay and linseed oil. The cooler may be made of S-bends, stoneware or fused quartz; for one furnace, there would be 5 rows of 4-inch S-bends, of which one is shown in the illustration; these pipes are cooled by a small amount of water trickling over them.

In some installations the towers are supplemented by Cellarius vessels of stoneware, about 46 inches long by 28 inches across, for acid cooling and adsorption (*see* Fig. 24). The design of this vessel provides for max-

imum absorption surface to a given total volume of solution. The function of the cooler S-bends may be performed by the Cellarius for gas cooling, of the same dimensions as just stated, but constructed in the opposite sense, so that it holds no liquid. The illustration (Fig. 24) will indicate the details.

Acid made by method (3) involves the removal of any unchlorinated hydrocarbon present in vapor form, then absorbing hydrogen chloride in water in a continuous system. For the recovery of hydrochloric acid obtained as by-product of pentane chlorination, a plant has been described.[18a]

Acid made by method (2), namely by burning chlorine in hydrogen, absorbed in towers with iron-free packing, is a water-white acid, essentially chemically pure. It more than meets the requirements for the chemist's C.P. acid. A patented method [19] avoids an excess of hydrogen with the consequent necessity of scrubbing the gas to be reworked, by using the undiluted gases in a system closed as to escape gases.

Acid made by method (1) has a pale yellow color; it is shipped in glass carboys of 12-gallon capacity, set in a wooden protecting box, or in rubber-lined wooden tanks, four tanks to a flat railroad car, or, to a lesser extent, in steel tanks lined with wood impregnated with a wax tar. The content of arsenic is usually 0.0002 per cent As_2O_3 in the commercial acid; this low figure is due to the use of contact sulfuric acid which is made from carefully purified sulfur dioxide gas, itself obtained from selected ore or from sulfur. For certain purposes a still purer acid must be furnished; from the pot stills, an acid is made with an arsenic content of 0.00005 per cent As_2O_3. The production in 1935 was 264,500 tons of 20° Bé. acid or its equivalent, and the market price $18.10 a ton.

To illustrate the relative importance of the different processes, the following partial 1935 figures are given: hydrochloric acid 20° Bé. made from salt, 145,000 tons, from chlorine, 9950 tons, by-product and other, 14,000 tons.

Hydrochloric acid is used to clean steel before galvanizing (dipping in melted zinc), in wire steel plants, in the manufacture of dyes, and for a number of minor purposes.

GLAUBER SALT

Glauber Salt ($Na_2SO_4.10H_2O$) is a purified salt cake; the Glauber plant is usually adjacent to the salt cake storage bin.

Salt cake is dissolved in hot water, best in a circular wooden tank with stirrer. Steam is passed in during the solution to make up for cooling to the air. The solution is made as strong as possible (32° Bé. hot), lime is added to neutralize the sulfuric acid invariably present, and to precipitate iron hydroxide and alumina. The liquor is allowed

[18a] "High-boiling solvents from natural gas pentanes," Lee H. Clark, *Ind. Eng. Chem.*, **22**, 439 (1930), with 2 flow-sheets.
[19] U. S. Patent 1,414,762; *see also* N. A. Laury, "Hydrochloric acid and sodium sulfate," New York, Chemical Catalog Co., Inc., 1927, Chapter 8.

to settle, and the clear portion is run into the crystallizers. The mother bottom is filter-pressed, and the filtrate sent to the crystallizers.

The latter are usually wooden forms lined with lead, 15 feet long, 6 feet wide, and 2 feet deep. On standing over night, crystals form; in the morning the mother liquor is run off by removing a wooden plug from the outlet in the bottom of the crystallizer, and the crystals shoveled into low trucks on wheels; these are pushed to one of several openings in the floor, through which the crystals are dumped into the storage bin and shipping room below. The mother liquor is collected in a low tank and pumped into the dissolver, replacing, after being heated, a part of the water.

The crop of crystals in the winter months is greater than in the summer; in fact during hot spells it happens that no crystals at all form. For this reason, a stock of crystals is accumulated in the winter and spring, and stored in bins closed on all sides. Ventilation must be avoided, for Glauber salt loses its water of crystallization on exposure to the air.

Glauber salt is crystallized from an acid liquor, in order to obtain colorless crystals; from a neutral liquor, slightly colored brown crystals form. The composition is:

	Per Cent
$Na_2SO_4, 10H_2O$	97.52
$NaCl.$	.21
Moisture	2.23
$Fe_2(SO_4)_3$	.01
$CaSO_4$	.022
Free acid	.008

In a few plants, iron crystallizers are used, and the liquor is kept alkaline; this results in a product slightly off color.

Glauber salt is used extensively in the textile industry; in 1935, 40,735 tons of Glauber salt were produced; the market price was $13.48 a ton. Its manufacture is interesting not only because of the high purity obtained but because, by making the first hot solution strong enough, no concentration of any kind is needed. This principle is followed in the chemical industries whenever possible.

SODIUM SILICATE

Sodium silicate is made by fusing together sand and soda ash in the proportions of 100 pounds of sand to 52 pounds of soda ash. Its formula is somewhat indefinite; it lies between $Na_2O.3SiO_2$ and $Na_2O.4SiO_2$. It occurs chiefly as a thick syrup, a water solution of the solid (30° to 40° Bé.). Sodium silicate is commonly called water glass, because when solid it is a glass, and because this glass, unlike the lime-soda glass, ordinary window glass, is soluble in water. The melting is performed in large tank furnaces similar to the window-glass furnace.[20] The materials are introduced in batches, at intervals; the product may be drawn

[20] Chapter 11.

off continuously or periodically. A mixture of sodium sulfate and coal may be used instead of part of the soda ash.

As the melt leaves the furnace, a stream of cold water shatters it to fragments; these are dissolved by means of superheated steam in tall, rather narrow steel cylinders with false bottoms,[21] and the resulting liquor clarified.[22] Sodium silicates are sold in solutions which vary from the most viscous, 69° Bé., to thinner ones, reaching finally 22° Bé. solutions, adapted for paints. The dry material in the form of a powder is also on the market, and is made by forcing the thick liquor through a very fine opening into a chamber swept by a rapid current of cold air, which carries off the moisture.[23] Because sodium silicate is hygroscopic, powdered sodium sulfate is sometimes incorporated with the solid silicate [24] to prevent caking. In composition, the sodium silicates may be varied from 1 $Na_2O \cdot 2/3$ SiO_2, to 1 $Na_2O \cdot 3.9$ SiO_2; they differ in alkalinity from p_H 13.2 for $Na_2O \cdot 2/3$ SiO_2, to p_H 10.8 for the $Na_2O \cdot 3.9$ SiO_2 silicate, measured in 1 per cent solutions. In the concentrated solutions, the p_H is not very different. Each of the commercial ratios results in a liquid with special properties, rendering it the proper selection for a specific purpose.[24a]

The uses of sodium silicate are surprisingly numerous; it is added in the crutching of soap [25]; it serves to impregnate wood, to weight silk, as a mordant, to clarify juices and solutions, to render bricks and cements non-porous, as a detergent, and as an adhesive, particularly in making corrugated paper boxes.

BROMINE AND BROMIDES

When the brines from which table and dairy salt is made contain bromides, the bromine may be recovered from the mother liquors. The oldest process, still in use, is to concentrate the mother liquor and to treat it in a stone still (untarred) with sulfuric acid and sodium chlorate (formerly with manganese dioxide); a current of steam carries off the bromine liberated. An earthenware coil receives the mixed steam and bromine and condenses both, by water cooling; two layers collect in the stoneware receiver; the lower one is the dark red, liquid bromine; the upper one, bromine water. They are separated, and the bromine, from the water layer may be recovered by blowing with air or natural gas. This lean bromine gas is treated separately; it is passed through a small stoneware tower filled with moist iron filings, and a strong solution of ferric bromide forms, from which the bromine is displaced by chlorine gas. Bromine is a liquid which boils at 63° C. (145° F.).

[21] U. S. Patent 1,138,595
[22] U. S. Patent 1,132,640.
[23] German Patent 249,222.
[24] U. S. Patent 1,139,741
[24a] Several interesting and instructive bulletins on this subject may be obtained by addressing the Philadelphia Quartz Company, Philadelphia, Pa. See also "Sodium metasilicate as an industrial alkali," James C. Vail, *Trans. Am. Inst. Chem. Eng.*, 25, 123 (1930).
[25] Chapter 32.

In another process the brine is treated directly with chlorine gas; still another process is based on the fact that on electrolyzing a bromide-bearing brine, the bromine is liberated first, the chlorine only later.

Crude bromine is purified from chlorine, its chief impurity, by a redistillation, passing the vapor over iron filings which retain the chlorine.[26]

Bromides are made by saturating caustic soda (for sodium bromide, NaBr) with bromine; a smaller amount of sodium bromate is simultaneously formed, $6NaOH + 3Br_2 = 5NaBr + NaBrO_3 + 3H_2O$. Bromides are valuable pharmaceuticals; bromine serves in the manufacture of certain dyes [27] as a disinfectant; its irritating and suffocating properties have led to its use as a war gas.[28]

At Wilmington, N. C., bromine is obtained from sea water,[28a] which contains 0.0064 per cent (average) of bromine; 1800 gallons of sea water must be treated for each pound of bromine obtained. This plant is now the largest American producer. It is obtained also at Midland and Saginaw, Michigan, in Ohio, and in West Virginia. A large part of the world's supply comes from Stassfurt, Germany. A salt deposit rich in bromides and readily flooded by controlled amounts of sea water occurs in Tunis.[29]

In 1935, 16,428,533 pounds of bromine were produced in the United States, valued at 21.2 cents a pound.

The use of ethylene bromide with tetraethyl lead as antiknock compound [30] has meant a large consumption, supplied first by imports, but more and more, by domestic producers. The increasing production of bromine has made this possible. In 1930, 3,024,484 pounds of ethylene bromide were imported; in 1935, 477,005 pounds only had to be imported.

<center>OTHER PATENTS</center>

U. S. Patent 1,165,815 (1916) to Thelen and Wolf, on a mechanically operated salt-cake furnace; German Patent 325,314, on preheating the charge for the Mannheim furnace; German Patent 295,073, to Henry Howard, of Massachusetts, on serving salt and sulfuric acid direct to Mannheim furnace. U. S. Patent 1,907,987, soda ash; 1,940,459, manufacturing soda ash; 2,035,441, apparatus for manufacture of sodium carbonate monohydrate; 2,038,025, sodium sesquicarbonate from bicarbonate; 1,928,540, manufacture of sodium bicarbonate; 1,921,505, low apparent density sodium carbonate; 1,868,949, sodium sulfate production; English Patent 375,039, electric heat for the salt-sulfuric acid reaction; German Patent 489,917 and 516,348, mechanical salt cake furnace; U. S. Patent 1,853,330, distillation and concentration of hydrochloric acid; German Patent 558,553, same, with the aid of added $CaCl_2$; German Patent 535,355, same, and recovery of acetic acid and HCl from the same vapors; 1,902,801, continuous process of preparing liquid bromine; 1,917,762, extracting bromine from dilute solutions; 1,930,143, bromine recovery from spent developers; 1,919,721, preparation of bromates.

[26] A list of patents relating to these various processes will be found on page 93. *Dept. Interior Bull.* **No. 146;** see reading references; the first two patents were U. S. Patents No. 460,370 (1891) and No. 11,232 (reissue 1892).

[27] Thus eosine, Chapter 28.

[28] Chapter 34.

[28a] "Commercial extraction of bromine from sea-water," Leroy C. Stewart, *Ind. Eng. Chem.*, **26,** 361-369 (1934), with 20 illustrations.

[29] "The future demand for bromine," C. R. De Long, *Ind. Eng. Chem.*, **18,** 425 (1926).

[30] Chapter 24.

PROBLEMS

1. (a) A plant intends to manufacture 300 tons of Solvay ammonia soda per day; the soda to be 98.8 per cent Na_2CO_3. How much salt will be required per day, if its NaCl content is 99 per cent, for the actual conversion? How much salt is required since the carbonating towers consume 66 per cent of the salt, the rest being wasted? At what point or points is the salt lost which is not used? (b) What is the weight of the bicarbonate of soda made as intermediate product?

2. The ammonia NH_3 which takes part in the reaction is about one-third the weight of the soda ash produced. For the production of the soda ash specified in Problem 1, how much carbon dioxide is needed for the actual final product, and how much limestone, 95 per cent $CaCO_3$, must be calcined in order to obtain it? Is the lime obtained simultaneously sufficient for the regeneration of the fixed ammonia, or is it an excess, or is there a deficiency? (Leave fire gases in kiln out of consideration.)

3. Referring to Problems 1 and 2, let there be once again the amount of ammonia in process as found to have reacted, mainly in the absorbers, and some in the tower liquor and filtrate from the bicarbonate. How much would the ammonia be worth (at 5 cents a pound NH_3), compared to the value of the soda ash produced? The amount of carbon dioxide in process is again as much as leaves the plant in the soda ash, mainly returned from the calciner. How much calcium chloride in solution form leaves the ammonia still, in its run-off?

4. A plant manufactures soda of 99.5 per cent purity. The amount of salt actually transformed in the operation is 37 tons. The reaction $NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$ takes place to the extent of 75 per cent. How much salt is taken originally, how much left unused; what is the tonnage of soda ash made, if the calcination is performed without loss? What is the weight of bicarbonate of sodium, expressed as dry $NaHCO_3$?

5. In a Mannheim furnace, there are charged per day 6500 pounds of salt mixed with a certain amount of nitre cake. If the nitre cake has the theoretical composition for $NaHSO_4$, how many pounds of the latter must be charged per hour? Assuming the recovery of salt cake to be 98 per cent, how many tons of salt cake will be collected per day?

6. From the salt charged as described in Problem 5, hydrochloric acid is recovered with an efficiency of 89 per cent; it is made into 31 per cent HCl (about 20° Bé.). How many pounds of acid will be collected per day?

7. 4100 pounds of 96.5 per cent salt cake is made into Glauber salt, which has the analysis shown in the text. How many pounds of Glauber salt will be obtained, assuming that the mother liquors are worked up constantly so that the yield is 94 per cent? What will be the factor, salt cake to Glauber salt? (1 lb. salt cake produces x lbs. Glauber salt.)

8. It is desired to prepare 9 tons of sodium silicate syrupy, to test 38.8° Bé. The composition of the dissolved silicate is to correspond to $Na_2O \cdot 3.36SiO_2$. The specific gravity given corresponds to 36 per cent of the 3.36 silicate. How much soda ash 99 per cent, and how much sand 100 per cent will be required, the yield being assumed to be 92 per cent?

9. A brine is saturated and contains on analysis NaCl 298 grams per liter; $CaSO_4$ 5.1 g.p.l.; $CaCl_2$ .81 g.p.l.; $CaCO_3$ .15 g.p.l.; $MgCl_2$ .48 g.p.l. The non-NaCl materials restrict the amount of NaCl which the equal brine would hold at saturation. If that amount of salt is proportional to the equivalent of the foreign salts, what is the amount of NaCl which the brine will hold at saturation?

10. The crude Solvay $NaHCO_3$ crystals always contain ammonium in the ratio of 5 NH_4 to 95 Na, and it cannot be washed out; it is assumed that a double salt forms. It is only on calcining that the ammonia is liberated. NaCl and Na_2SO_4 on the other hand wash out readily at the filter. For the weight of bicarbonate in Problem 1 (b), and in Problem 4, how much ammonia does that represent per day? In what way is it saved to the system?

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"The culture of certain silicate gardens," James G. Vail, *Ind. Eng. Chem.*, 26, 113 (1934).

"Glauber salt in North Dakota," Irvin Lavine, Herman Feinstein and Earl Skene, *Chem. Met. Eng.*, 42, 681 (1935).

"Die Sodafabrikation nach dem Solvay-Verfahren," Julius Kirchner, Leipzig, S. Hirzel, 1930.

Wherever possible the salts of sodium are used in preference to the salts of other metals, for the salts of sodium are soluble and cheap. The cheapness is due to the abundance of common salt, NaCl, the source (as to metal) of nearly all other sodium salts.

Chapter 4

Sodium Sulfide, Sodium Thiosulfate (Hypo), Anhydrous Bisulfite of Sodium, Sodium Hyposulfite

In a modern chemical establishment manufacturing a number of heavy chemicals for the general trade, there is a relation between the various sections in that the product of one becomes the raw material for the next. The sulfuric acid, the first product, is the only exception; it is made entirely from purchased materials (sulfur or pyrite), or from by-product sulfur dioxide gas from a smelter. The preparation of nitric acid from sulfuric acid and sodium nitrate was accompanied by the production of nitre cake, and this must be supplemented by its manufacture from salt and acid in the pot stills; the nitre cake fused with salt gives hydrochloric acid and salt cake (Na_2SO_4). A large amount of salt cake is sold as such; the remainder is heated with coal or coke and made into sodium sulfide, Na_2S, with by-products of sodium carbonate, Na_2CO_3, and sodium sulfite, Na_2SO_3, which are properly worked up into sodium thiosulfate, $Na_2S_2O_3$, usually called "hypo" from its old name of hyposulfite, now abandoned. Not all sodium sulfide is made from salt cake, for while the latter is the cheapest raw material, furnaces, leaching tanks, and other equipment are required; for small-scale operations, soda ash and sulfur are more suitable. In large plants, such as the one described above, caustic soda, chlorine, and soda ash are not usually included, but all those products which require sulfuric acid for their manufacture [1] are part of the plant. Soda ash is usually purchased in considerable quantities, for it serves to make anhydrous bisulfite of soda, $NaHSO_3$, sodium hyposulfite (hydrosulfite), $Na_2S_2O_4$, and in many cases, sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$; plants for these three products properly belong to such an establishment which includes the manufacture of sulfuric acid, because the sulfur dioxide which they require may be taken from the burner house by simply erecting a pipe line. To complete the description, a power house for steam and electric current generation would be included; also water pumps for cooling, washing, and absorbing water; shipping facilities, and offices.

A modification of the set-up outlined will make good the lack of nitre cake, and sodium sulfate from nitre cake, by purchasing natural sodium sulfate. The nitric acid would then also have to be purchased from synthetic ammonia plants, or the ammonia might be purchased, and the oxidation performed in the old nitric plant, remodeled for the purpose.

[1] Chapter 2; but not superphosphate (Chapter 7), which is a specialty.

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SODIUM SULFIDE

Sodium sulfide, Na_2S, has become extremely important as a depilatory,[2] in the manufacture of sulfur dyes, and, in solution, as a solvent for the same sulfur dyes.[3] It was formerly produced altogether in the form of crystals, $Na_2S.9H_2O$, which in the commercial form contained about 30 per cent Na_2S; the crystals are brown, while pure sodium sulfide crystals are colorless. These crystals are still made, but the greater part of the sulfide is now marketed in the form of concentrated sodium sulfide with 60 per cent Na_2S, as solid cakes and lumps, or as flakes ("chips"). The method may be outlined as follows: Salt cake (or roast cake) from the Mannheim furnace mixed with coal is heated in a reverberatory furnace; a melt is produced which is raked out and either dissolved in water at once, or allowed to cool to solid cakes which are later leached with hot water. The solution is made strong enough
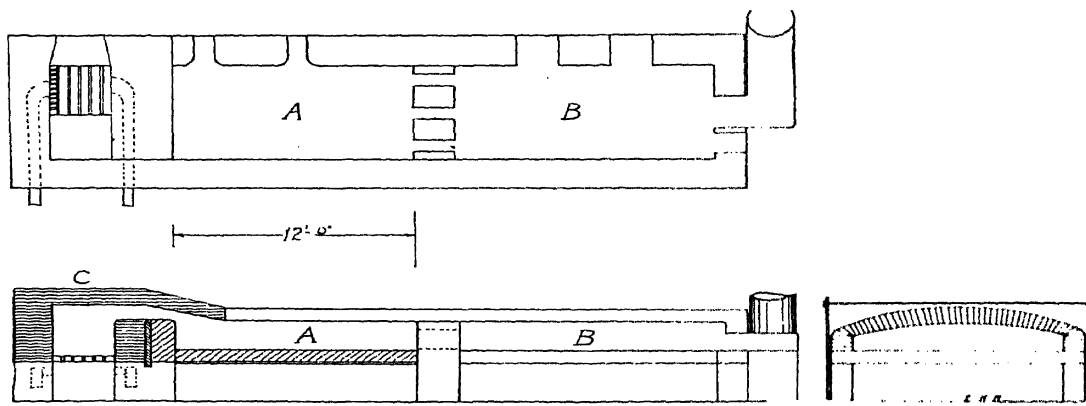
FIGURE 26.—Sodium sulfide furnace, reverberatory type; *A*, reduction hearth; *B*, preheating chamber. The fireplace and half of the bridge wall are of hard firebricks, *C*; the hearth of alunite or aluminate bricks.

so that on cooling in shallow pans, crystals of $Na_2S.9H_2O$ form. In order to produce the 60 per cent sulfide, the crystals are melted in special pots and water driven off from the hot liquid; on cooling a black solid with red fracture forms. Another way consists of boiling down the first solution after filtering or settling, until the sodium sulfide content is a little above 60 per cent.

Reverberatory Furnace. A reverberatory furnace is shown in Figure 26; it is a low arch furnace with a fireplace separated from the hearth by a bridge wall. The fire gases strike the roof over the fireplace and are deflected onto the charge on the hearth; the low arch forces intimate contact between fire gases and charge. From the furnace proper the gases pass to the preheating chamber, of dimensions similar to those of the

[2] Chapter 36.
[3] Chapter 28.

hearth, and from there to the stack. For a furnace whose hearth is 12 feet long and 8 feet wide, the charge is 1000 pounds of salt cake [4] and 500 pounds of coal screenings. Such a charge is shoveled into the rear of preheating chamber, where it is warmed by the outgoing gases for an hour. It is then pushed with a hoe to the working hearth and heated there, with occasional stirring, for another hour, when it is ready to be pulled out. Instead of shoveling in the charge, it may be fed in from an overhead bin through an opening in the arch. Melted sulfide is extremely corrosive, so that the construction of the furnace is a special one. The floor of the hearth consists of alunite or other basic bricks, set upright on their smallest face. These bricks rest on several thicknesses of asbestos paper soaked in silicate of soda solution; such an underlining has been found efficient in preventing the escape of melt. The alunite bricks are placed in a solution of silicate of soda for some hours just before laying. The hearth side of the bridge wall is also lined with alunite bricks, while the fireplace side and the arch over the whole furnace are of ordinary fire bricks. The rear wall is usually lined with a hard firebrick. Such a furnace will last 8 to 12 months, when it must be rebuilt.

In order to insure a high yield the atmosphere in the furnace must be a reducing one; the fire gases should contain one or several per cent carbon monoxide and no oxygen. Such fire gases are obtained by building a deep bed of coal on a fireplace of rather small dimensions, using soft coal and forced draft. The reactions on the hearth are:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$
$$Na_2SO_4 + 4CO = Na_2S + 4CO_2.$$
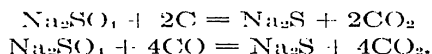
There are several ways in which the melt may be handled on leaving the furnace. A simple and efficient way is to pull the charge into 8 or 10 buggies on wheels, each holding 80 to 100 pounds so that one man can handle them. Another way is to pull the charge into two steel boxes on low trucks. In either case the melt is allowed to cool; during the cooling of the cakes, some further reduction takes place. The cold cake is broken with a sledge and fed to an edge runner [5] washed by a constant flow of warm water. A solution of sodium sulfide with suspended matter results, which is elevated to a settling tank. In the older plants, the cake is fed to a jaw crusher [5] in the floor, then elevated to one of four leaching tanks which are worked in series; each tank accommodates one day's melt. The fresh melt is wetted with the wash from the melt of the day before, and this wash in turn has first rested on the nearly spent melt of two days before; the fourth tank is being emptied. In this way each melt is leached three times.

A totally different way is to pull the melt into a ladle and to bring it over a dissolving tank with stirrer. The fluid melt, still hot, is run

[4] Instead of salt cake, nitre cake was formerly used; the escaping sulfuric acid caused a cloud at the top of the stack, which caused much difficulty with municipalities. It was thought that by substituting salt cake, the cloud would vanish; but to everybody's surprise, it continued. In this case, it is due to sublimed sodium salts; these may be removed from the stack gases by a Cottrell precipitator; *see* Chapter 43.

[5] Chapter 44.

into the water which is thereby heated; this operation is extremely noisy. It utilizes a part of the heat of the melt, however, and saves labor, so that it will probably become standard, at least for the large plants. The suspension may be settled or filter-pressed using iron wire filter cloth; the press cake is made up with water once more, filter pressed again, and the filtrate used in the dissolving tank.

The melt in the cakes is 60 to 65 per cent Na_2S; such rich melts flow less easily than melts contaminated with unreduced sulfate or with carbonate.

The sulfide liquor obtained by any of these variations is hot, and of such strength that after being run into shallow iron pans, crystals deposit over night. The mother liquor contains sulfide, and also sulfate, sulfite, and carbonate; it may be concentrated, when all the salts other than sulfide precipitate, leaving a concentrated solution of sulfide which may usually be crystallized; in some cases it may contain so much silicate that it will not crystallize. The precipitated salts are dissolved in water and the solution used for making thiosulfate. The brown crystals with 30 per cent Na_2S may be sold as such, or they may be placed in iron pots over a fire, melted, and enough water removed to raise the content of Na_2S to 60 per cent. The liquor may be run into concentrating pans directly and evaporated to the higher strength; the difficulty in that case is that the sulfate, carbonate, and similar impurities deposit during the concentration and coat the bottom of the concentrating pans, causing them to become locally overheated which results in leaks.

The 60 per cent liquor may be run into shallow flat pans, where it solidifies over night; it is then broken and shipped as lumps. There are many other ways to fix the final shape of the product; the best one is to feed a thin layer to a water-cooled rotating drum, actuated by means of a ratchet; a knife detaches the cake, and the thin strips fall and break into still smaller flakes, called chip sulfide.[6] In this form, solution at the consumer's plant is greatly facilitated. The color of chip sulfide is red; like any other form of sulfide it must be stored in air-tight thin steel drums, otherwise it turns green due to the formation of sulfate and carbonate.

New Types of Sulfide Furnaces. The old reverberatory furnace is still the most reliable way to manufacture sulfide, although many proposals for new types of furnace have been made. The aim of the newer furnaces is to reduce labor to a minimum by a continuous operation largely automatic. On one of these furnaces, a rotary style [7] is proposed with carbon monoxide gas, prepared in auxiliary vessels, as reducing agent and fuel. Several German proposals are promising also; one [8] involves the use of a Bessemer pear such as is used for making steel, and still another [9] proposes ovens with pendulum or shaking motion. Two blast furnaces have been patented; one proposal [10] allows the

[6] U. S. Patent 915,633.
[7] U S. Patent 1,397,497.
[8] German Patent 388,545.
[9] German Patent 389,238.
[10] German Patent 255,029.

melt to solidify; in the other [11] the fluid melt is either tapped at intervals or drawn off continuously. In the latter furnace, as well as in one proposed by H. K. Moore,[12] the fluid melt is dropped at once into a "quench tank". Finally, studies in the application of the electric furnace to the manufacture of sodium sulfide have been made [13] and applied commercially in Italy during the war.

SODIUM THIOSULFATE

Sodium thiosulfate [14] $Na_2S_2O_3.5H_2O$ or "hypo" is the agent employed in photography for dissolving the unreduced silver salts, and in textile mills as an "antichlor". It is made in two ways; the first one is independent of any other process, and requires soda ash and brimstone; the second makes use of by-product sulfide liquors and is dependent upon a sulfide plant; its sulfur dioxide may be drawn from the burner house of the sulfuric acid plant generally forming part of a large establishment. It is customary in the second kind of plant to have in reserve soda ash and brimstone so that in case the by-product liquor fails, these materials may be used instead. The same apparatus serves without any change, and burner gas is the source of sulfur dioxide, as before.

The Soda Ash-Brimstone Process. Soda ash is dissolved in hot water and the solution (26° Bé.) pumped to a small storage tank at the top of the first of two absorption towers. These are of lead supported on wooden beams, and are filled with hardwood sticks except in the lower part where a small chamber of hard acid bricks is provided. The nearly spent sulfur gas from the second tower (second with respect to the liquor) enters at the base and meets the descending soda ash solution which absorbs all the remaining sulfur dioxide. The partly gassed liquor from the first tower is elevated to the top of the second tower wherein it meets the sulfur dioxide gas fresh from the burners; the soda ash is completely changed to sodium bisulfite, which runs out through a seal at the base of the tower and is collected in lead-lined receiving tanks.

$$Na_2CO_3 + H_2O + 2SO_2 = 2NaHSO_3 + CO_2.$$

The accompanying illustration (Fig. 27) indicates the dimensions and disposition of the apparatus. The nitrogen, oxygen, and carbon dioxide pass out of the first tower to a small stack.

Sulfur dioxide may be made by burning brimstone in iron pans cooled from below by air, and set in brick work; or, a special patent burner may be installed, such as the Glen Falls (N. Y.) rotary burner, the Chemico spray burner (Chapter 1), the Vesuvius burner with shelves, and others.

Formerly the bisulfite liquor, with 22 per cent SO_2 content, was an important product; it has been replaced by the anhydrous bisulfite of soda, a powder with 60 per cent SO_2, described further on. By means of soda

[11] German Patent 273,878.
[12] U. S. Patent 1,130,317.
[13] *Chem. Abstracts,* **15**, 3423 (1921).
[14] An old name for the same subtsance is sodium hyposulfite, from which the name "hypo" originated.

ash, the bisulfite liquor is changed into neutral sulfite, and this is heated with powdered brimstone [15] in a brick-lined cast-iron vessel with stirrer. A solution of sodium thiosulfate results; it is concentrated in a boiler from 36° Bé. to 51° Bé. hot. After settling, this liquor is run into lead-lined or steel crystallizers and allowed to cool. When iron crystallizers are used, a crust of the crystals is left on the sides and bottom to avoid contamination

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + H_2O + CO_2$$
$$Na_2SO_3 + S = Na_2S_2O_3.$$
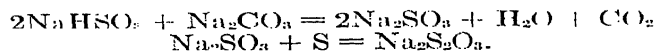
After two or more days, the mother liquor is run off, the crystals are shoveled to centrifugals which remove adhering mother liquor, washed
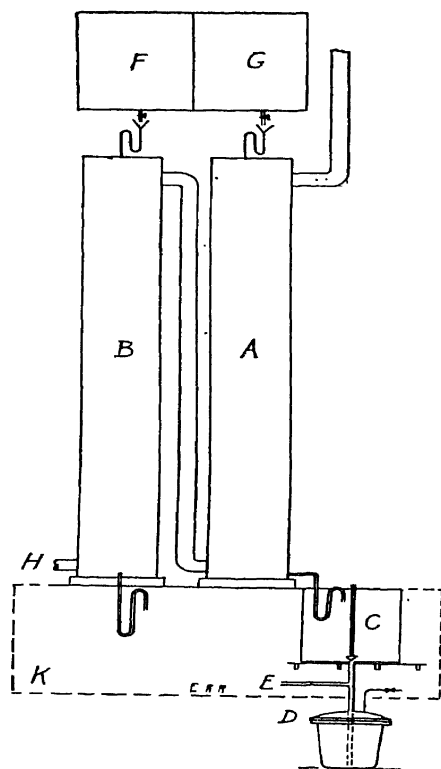
FIGURE 27.—Plant for making sodium bisulfite solution. Soda ash solution in tank *G* is fed to the first tower, *A*, where it meets the weak gas from the top of the second tower, *B*. The liquor from *A* collects in *C*, is run into the lead-lined cast-iron pot *D* and forced through *E* to tank *F*, from which it is fed to tower *B*, meeting fresh gas entering at *H*. The finished liquor collects in the storage tank *K*.

by a short spraying from a hose, and dumped to a conveyor leading to the interior of a cylindrical steel wire screen. The screen consists of two sizes, a six-mesh half which receives the unassorted crystals, and a three-mesh screen which forms the rear half.[16] The fines drop through the six-mesh wire as the screen slowly rotates; the pea size drops through the three-

[15] The crushing of brimstone is not without danger.
[16] *Compare* Chapter 44

mesh wire, while the coarser pieces, the "crystal" size, roll off at the far end of the wire.   No drying of the crystals is necessary.

A fine crystal product of uniform size called "granulated hypo" is made by cooling the 51° Bé. liquor in circular steel pans 10 feet in diameter and 3 feet deep, in which a two-armed scraper slowly revolves while the liquor cools.

Sodium thiosulfate crystals effloresce so readily in air that they must be packed at once in air-tight containers, cartons or paper-lined barrels.

The By-Product Sulfide Liquor Process.   The carbonate and sulfite which separate from the sulfide liquor while it is in process of concentration are made up with water; the adhering sulfide is also dissolved.   This liquor becomes the raw material for the sodium thiosulfate manufacture. In the plants which filter the suspension from the "quench tanks", and make up the first mud with water again, then filter once more, this second filtrate becomes the raw material for hypo; the first filtrate is essentially sulfide.   The most satisfactory relation of the carbonate and sulfide (the sulfide is usually very low) is about 8 per cent Na_2S and 6 per cent Na_2CO_3, when the reaction

$$2Na_2S + Na_2CO_3 + 4SO_2 = 3Na_2S_2O_3 + CO_2$$
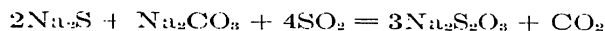
takes place during the gassing period.   An excess sulfide over this amount must be avoided, as it may lead to a loss of useful materials in the generation of H_2S;

$$Na_2S + SO_2 + H_2O = Na_2SO_3 + H_2S.$$
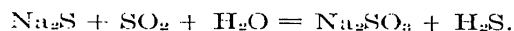
Some of this hydrogen sulfide will be changed into sulfur by sulfur dioxide, but it is manifestly cheaper to supply sulfur in the form of brimstone, if any is needed.   Technical sodium sulfide always contains some polysulfides, and these supply some sulfur which reacts with such sulfite as may be present in the original liquor.   Should the carbonate run high and the sulfur low, brimstone may be added to change the sulfite formed (the bisulfite is avoided [17]) into thiosulfate.

The sulfide-carbonate liquor may be treated with sulfur dioxide gas, the regular burner gas with 7 per cent SO_2, in towers.   Instead of a single passage of the liquor through a rather tall tower, many passages through a shorter tower may be substituted; these are then called circulating towers.   The liquor is run into a large tank and pumped at a rapid rate to the top of the tower, which has wooden shelves.   As the liquor cascades from shelf to shelf, fresh surfaces are exposed and the absorbing liquid exhausts the gas readily.   The gassed liquor at the base of the tower runs back into the original tank.   The tower may be 20 feet high, 4 feet in diameter, of steel lined with bricks; the wooden shelves are perhaps 10 inches apart.   Each shelf covers only about two-thirds of a circle, and the openings are staggered, so that the liquor changes

[17] Acidity due to $NaHSO_3$ is detected and measured by a titration with caustic in presence of phenolphthalein; Na_2SO_3 is neutral to phenolphthalein, but alkaline to methyl orange; it is measured, with any carbonate present, by a titration with standard acid, in the presence of methyl orange; $NaHSO_3$ is neutral to methyl orange.

direction constantly. Two or more towers may be used, the gas passing from one to the other to insure it exhaustion.

After sufficient gassing, the liquor is filter pressed through cotton duck cloth and concentrated in a steel boiler with steam chest.[18] The crystallization and further steps are the same as described under the soda-ash brimstone process. It will be noted that in normal running the sulfide by-product liquor requires no brimstone addition.

In 1935, there were produced 24,477 tons of sodium thiosulfate, valued at $41.30 a ton.

ANHYDROUS BISULFITE OF SODIUM

The commercial methods [19] for manufacturing anhydrous bisulfite of sodium, $NaHSO_3$, a cream-colored crystalline powder, differ in detail, but are alike in the general principle, namely, in passing 7 or 8 per cent sulfur dioxide into a suspension of soda ash in the mother liquor saturated with sodium bisulfite [20] from previous batches. When starting a new plant, a suspension of soda ash in a saturated soda ash solution may be used There is produced a suspension of anhydrous bisulfite, which is passed through centrifugals; the wet powder remains, the mother liquor is collected in the "emulsion" tank and treated with soda ash to produce the suspension which is sent through the process again. The wet powder is dropped to a conveyor leading to a circular shelf drier with six shelves; rotating arms move the material from shelf to shelf, dropping it through alternate circumferential and central openings. The shelves are hollow steel, with steam circulation. The powder issues from the bottom warm and dry; a small inclined bucket conveyor lifts it into a hopper from which barrels are filled by pulling a slide.

By using a building with several stories, the moving of the material may be by gravity, except for feeding the soda ash to the emulsion tank, and lifting the soda ash emulsion to the absorbers. These operate in two stages; the first stage absorbers are on the top floor, receive the soda ash emulsion and the sulfur dioxide gas which has already passed through the second stage absorbers. These latter, on the floor below, receive the suspension from the first stage absorbers by gravity, and the fresh sulfur dioxide gas from the sulfur or pyrite burners. Here the soda ash is completely transformed to anhydrous bisulfite, and this suspension is fed to the centrifugals on the floor below, while the drier is on the lower floor, on a level with a railroad car floor.

The function of the drier is merely to remove adhering moisture; the anhydrous bisulfite is produced as such in the suspension.

$$Na_2CO_3 + 2SO_2 + H_2O \longrightarrow 2NaHSO_3 + CO_2.[21]$$

[18] Chapter 43.

[19] U. S. Patents 1,099,177; 1,084,436; 1,023,179.

[20] As soon as soda ash is added to the mother liquor, its sodium bisulfite is changed to sodium sulfite, and the suspension is soda ash in sodium sulfite solution.

[21] In Patent 1,023,179, the reaction is given as: $2NaHSO_3 + 2Na_2CO_3 + 2H_2O + 4SO_2 = 6NaHSO_3 + 2CO_2$. The product is therefore held to be solid bisulfite of sodium, $NaHSO_3$, which is known to exist. In many processes, however, it is more likely that the anhydride, $Na_2S_2O_5$, forms, for several samples from different manufacturers contained 61.9, 64.1, 63.5, 62.8 per cent SO_2 respectively.

The absorbers are steel tanks lined with bricks, 15 feet high and 15 feet in diameter; the tight-fitting closed top is cast-iron covered with lead. A 4-bladed hard lead propeller working through a stuffing box makes 100 revolutions per minute; the gas inlet pipe reaches about 1 foot below the liquid. A 10-inch main brings the gas, and 3-inch lines (3 to each tank) deliver it into the suspension. The spent gas from the first stage absorber is pulled out by a fan and discharged into the air. The propeller shaft is lead-covered, as is also the rod carrying the plug valve which closes the discharge hole in the bottom.

Anhydrous bisulfite of sodium is used in the manufacture of dyes, and in their application to fiber; as an "antichlor"; in the sterilization of casks for beer and other similar beverages, and in a number of other cases.

SODIUM HYPOSULFITE (HYDROSULFITE)

Sodium hyposulfite, $Na_2S_2O_4$, called hydrosulfite in the trade, is a convenient form of the powerful reducer which is used for the reduction of certain dyes; before its advent in the trade, it had to be prepared at the textile mills and used at once. Until recently, it had to be imported, chiefly from Germany; it is now manufactured in the United States.

The method [22] includes four steps. (1) Powdered zinc of 93 per cent purity is suspended in water in a lead container provided with cooling coils and a stirrer. Pure sulfur dioxide, best from a tank of liquid sulfur dioxide, now an article of commerce,[23] is led in, fast at first, and more slowly near saturation. The temperature is kept below 30° C. The color changes to black, to gray, finally to cream.

$$Zn + 2SO_2(H_2O) = ZnS_2O_4(H_2O).$$
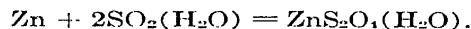
(2) The content of the saturator is transferred to a lead-lined steel tank, with stirrer; a soda ash solution is added, in slight excess over the amount indicated by the reaction

$$ZnS_2O_4 + Na_2CO_3 = ZnCO_3 + Na_2S_2O_4.$$
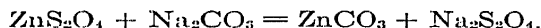
Zinc carbonate precipitates, while sodium hyposulfite remains in solution. The suspension is filtered by suction on a Nutsch [24]; the cake is washed several times, but only the first wash is added to the filtrate; the subsequent ones are pumped into the saturator.

(3) The filtrate reaches the salting-out tank; its strength is adjusted to 15 per cent $Na_2S_2O_4$, and to this liquor salt (NaCl) is added, 300 grams for each liter of solution. The hydrated sodium hyposulfite, $Na_2S_2O_4 \cdot 2H_2O$, separates in the form of needles. The suspension is heated rapidly to 60° C. and kept there until all the crystals have been

Sodium bisulfite contains only 61.5 per cent SO_2, and as a contamination of sulfate is always present, and sulfite at times, it is probable that in some cases the product is anhydride, whose content of sulfur dioxide SO_2 is 67.3 per cent.

[22] "Sodium hydrosulfite as a dry powder," L. A. Pratt, *Chem. Met. Eng.*, **31**, 11 (1924).

[23] Chapter 19.

[24] Chapter 42.

transformed to the anhydrous sodium hyposulfite, $Na_2S_2O_4$, a sand-like crystalline powder.[25] The crystals are allowed to settle, the supernatant liquor is run off, and hot denatured alcohol is added. (4) The crystals suspended in the alcohol are transferred to a steam-jacketed vacuum pan, the alcohol sucked off after settling, and three portions of alcohol run in so that no water might remain. By warming and causing a vacuum, the adhering alcohol is removed (and recovered), leaving in the pan the dry, sandy material, of light gray color, 90 per cent pure.

OTHER PATENTS

U. S. Patent 1,946,089, on anhydrous (85 per cent) sodium sulfide, granular, free-running, and with rapid solution in cold water; 2,018,359, depilatory agent; 2,024,624, depilatory method and apparatus.

PROBLEMS

1. A sulfide furnace receives a charge of 1000 pounds of salt cake per hour; theoretically, 549.5 pounds of Na_2S should be recovered, but the recovery is only 77 per cent. The product is made into chip containing exactly 62 per cent Na_2S. How many pounds of chip are produced per day? The salt cake is never pure; the calculation must be based on a content of 95 per cent Na_2SO_4.

2. Sodium thiosulfate crystals $Na_2S_2O_3 \cdot 5H_2O$ of 97 per cent purity are produced by the reaction $2Na_2S + Na_2CO_3 + 4SO_2 = 3Na_2S_2O_3 + CO_2$, from by-product liquor from the sodium sulfide process; the production of hypo crystals is 20,000 pounds per day. Assuming that the reaction takes place to the extent of 96 per cent, how many pounds of Na_2S, Na_2CO_3 and SO_2 will be required?

READING REFERENCES

"The manufacture of sodium thiosulphate," L. Hargreaves and A. C. Dunningham, *J. Soc. Chem. Ind.*, **42**, 147T (1923).

"Die Verfahren der anorganische chemische Industrie," zweites Berichtsjahr, Dr. W. Siegel, Berlin and Vienna, Urban und Schwarzenberg, 1935.

The patent and other literature as indicated in the text.

[25] The transition point of the hydrated salt to the anhydrous form is 52° C.

The manufacture of caustic soda directly from salt in solution, in a single operation, has passed, in the last forty years, from an exciting possibility to the humdrum of everyday technology. Caustic soda is a cheap, soluble alkali; lime is still cheaper, but is almost insoluble. Caustic soda is a strong alkali. Soda ash is a mild one; ammonia also.

Chapter 5

Caustic Soda and Chlorine

Caustic soda, NaOH, a white solid, extremely soluble in water, is made by the causticizing of soda ash by lime and by the electrolysis of salt, NaCl, in water solution, with the simultaneous production of chlorine and hydrogen. In the offing is a third method, namely, by the addiiton of sodium metal to a concentrated caustic solution, with certain precautions.

The production figures (U. S.) for the two main processes are:

	1936*	1935**	1933**
Caustic soda by lime-soda process....	456.000 tons	436,980 tons	439,363 tons
Caustic soda, electrolytic	369,000 tons	321,563 tons	247,620 tons

*Chem. Met. Eng., **44**, 77 (1937).
**Bureau of the Census.

CAUSTIC SODA BY CAUSTICIZING

Soda ash in the form of a 20 per cent solution is treated with milk of lime in slight excess, in a tank fitted with an agitator. The solution is warm (85° C.; 185° F.). After an hour, the agitator is stopped and the precipitated calcium carbonate settles; the strong (12 per cent NaOH) caustic liquor is decanted. Wash water is run into the agitator, and after some time, allowed to settle out its mud; the clear liquor is run off to the weak liquor tank. The mud is washed once more, yielding the "wash" which is run to the wash water tank. The mud is discharged from the tank; it may be carted to the dump, or it may be filtered and calcined, yielding a lime suitable for further causticizing. The first and second liquors are evaporated to 50 per cent NaOH concentration in single or multiple effect evaporators, and if solid caustic is desired, to the final strength of 98 per cent or better in cast iron pots over the free flame. In many plants, the 12 per cent NaOH liquor is used directly.

It has been found that choosing the concentrations of the reacting liquors as stated gives a good conversion (98 per cent) in the reaction $Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$, and yet does not impose too high a fuel cost for evaporation. The lime is slaked with just enough of the wash water to form the hydrate, and then only with as much more as is required to make the milk; so prepared, the rate of settling of the calcium carbonate is 1.5 feet per hour instead of 0.28, when making the milk at once. Using a rotary slaker, the rate of settling be-

comes 7.81 feet per hour.[1] In order to utilize all of the wash water, solid soda ash and the solid slaked lime may be fed into it.

Instead of batch operation, which the description just given presents, continuous operation may be secured, with classifiers for purifying the milk of lime, and thickeners to hasten settling. The two best-known systems are the Dorr and the Mount. In the study of the evaporation of the caustic liquor to high strengths, the use of diphenyl vapors around a nickel tube was found promising.[2]

An analysis of caustic soda made by causticizing soda ash manufactured by the ammonia soda process, has a low chloride content, an important consideration in many uses. The composition is:

	Per Cent
NaOH	98.62
NaCl	0.30
Na_2CO_3	0.90
Na_2SO_4	0.18
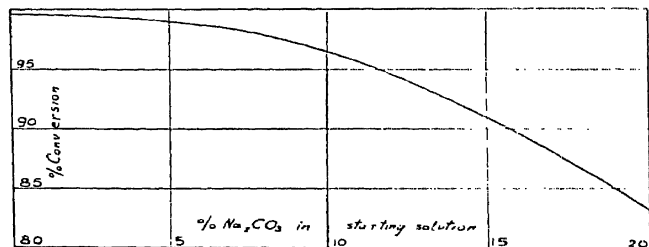
FIGURE 28. The conversion of soda ash to caustic by lime, for various concentrations of the soda ash in the starting liquor. The lime added is $Ca(OH)_2$ with no additional water. Example: Starting with a 10% Na_2CO_3 solution, 96.5% of the sodium carbonate will be converted.

CAUSTIC SODA BY ELECTROLYSIS

In point of tonnage, electrolytic caustic soda is inferior to caustic by causticizing; it represents, however, a totally different method of working, namely, the application of the electrical current to chemical decompositions and regroupings.

Many cells have been devised in which the decomposition may be performed; they may be listed under three heads: the diaphragm cells, the mercury cells, without diaphragm, and the bell-jar type, without diaphragm and without mercury. The first diaphragm cell was the Townsend cell, which is represented in modified forms by the Allen-Moore, Nelson, Vorce, Hooker, Marsh, and other cells. The original mercury cell was the Castner, still in use in the United States; modifications of it, giving good service, are the Whiting and the Solvay. An important representative of the bell-jar type is the Billiter cell.

For all cells it is customary to purify the salt solution and to employ it as strong as possible, that is, not far from saturated, about 25 per cent NaCl. For the diaphragm cells, the manufacture, described in a few words, consists of the preparation and purification of the saturated

[1] W. E. Piper, *Am. Inst. Chem. Eng.*, **24,** 1 (1930).
[2] W. L. Badger, C. C. Monrad and H. W. Diamond, *Am. Inst. Chem. Eng.*, **24,** 56 (1930)

salt solution, of the electrolysis of this solution in the cell wherein half the salt is transformed into caustic, of the concentration of this mixed solution with separation of the salt as the concentration rises, and of the final evaporation to the anhydrous caustic over the open fire. For the mercury cells, the procedure is about the same, but the caustic liquor issuing from the cell is free from salt. This is an important advantage if the liquor is to be used on the spot: it requires no concentration, for a salt content need not be removed. The liquor issuing from the diaphragm cell, with as much salt as caustic, could not be used as such for most purposes. For the manufacture of solid caustic, this advantage disappears. The diaphragm cells produce a final caustic with 2 per cent NaCl; this small amount is not objectionable for the important applications of caustic. The great purity in this respect of caustic from mercury cells (0.2 per cent NaCl) does not bring it a premium. The general procedure for the bell-jar type cells is similar to that for the diaphragm cells.

The decomposition efficiency of cells varies between 50 and 60 per cent; a high figure is the more important the dearer the electrical energy purchased. Decomposition efficiency is the ratio of the salt decomposed to the total salt; thus if 6 parts of salt are decomposed into caustic, and there remain 4 parts of salt unchanged in the liquor (both determined by titration), the decomposition efficiency is 60 per cent. The decomposition voltage for commercial cells lies between 3.5 and 5, with 4.5 perhaps an average. The theoretical decomposition voltage for NaCl is 2.25.[3] The voltage efficiency is the theoretical decomposition voltage divided by the actual decomposition voltage, here $2.25 \div 4.5 \times 100 = 50\%$. The actual voltage applied will vary with the current density, that is, the number of amperes per square unit of surface of electrode; the higher the current density, the higher the voltage necessary. A part of the difference in energy represented by the voltage figures appears as heat; the temperature of the diaphragm cell, for instance, maintains itself at about 60° C. In general, the rough estimate is made that the potential drop for each cell is 5 volts.

The current efficiency, or better, the cathodic current efficiency, varies from 90 to 96 per cent in the best-designed cells, under even running; it may drop to 75 per cent or even less, for a variety of causes. The cathodic current efficiency is the weight of caustic formed divided by the theoretical weight of caustic which the amount of current per hour (ampere hour, independent of voltage) should have formed (1.491 grams), multiplied by 100.[4]

The energy efficiency is the product of the voltage efficiency and the current efficiency, here $0.96 \times 0.50 \times 100 = 48\%$.

[3] This value is based on the Gibbs-Helmholtz equation, and takes into account the heats of formation of the substances represented in the equation $NaCl + H_2O = NaOH + \frac{1}{2}Cl_2 + \frac{1}{2}H_2$. A consideration of single potentials is misleading; among other things it leaves out of account the fact that there are 10^8 sodium ions to each hydrogen ion. Some hydrogen is undoubtedly deposited directly, but in amounts too small to matter. The bulk of the hydrogen is due to the secondary reaction of metallic sodium atoms on water.

[4] *Compare* "The fundamentals of electrolytic diaphragm cells," by H. K. Moore, *Am. Inst. Chem. Eng.*, **13**, I, 42 (1920).

The amount of current required to liberate a gram-equivalent at each pole is the Faraday, which is equal to 96,580 coulombs (1 coulomb = 1 ampere-second). One ampere hour equals 3600 coulombs, so that the amount of material liberated by 1 ampere-hour is:

$$\text{Chlorine } \frac{3600}{96,580} \times 35.46 = 1.3218 \text{ grams}$$

$$\text{Caustic } \frac{3600}{96,580} \times 40.01 = 1.4913 \text{ grams}$$

THE ELECTROLYTIC CELL

The two cells in the illustration (Fig. 29) show the essential parts. The current, which is always direct current, is said to enter at the anode and to leave at the cathode.[5] In a brine, there are present sodium ions Na^+ and chlorine ions, Cl^-. The chlorine ions give up their negative charge (one electron) at the anode, and become yellow chlorine gas, Cl_2.
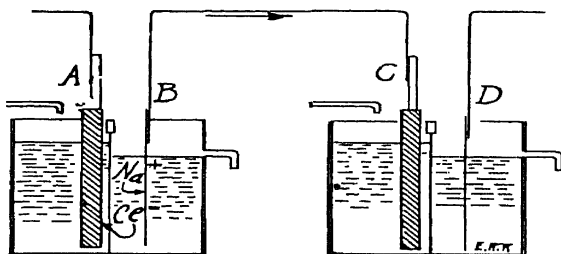
FIGURE 29.—Electrolytic cells for sodium chloride solution. The chlorine anion, Cl, forms chlorine gas at the anodes, marked *A* and *C*; the sodium cation, Na^+, forms sodium at the cathodes, marked *B* and *D*. A diaphragm divides the anode brine compartment from the cathode compartment.

The sodium ions receive a negative charge at the cathode and become sodium metal; this dissolves as such in the mercury (or lead) of the mercury type cell, or in the case of the diaphragm cell, a secondary reaction takes place, the sodium decomposing water to form sodium hydroxide and hydrogen gas: $2Na + 2H_2O = 2NaOH + H_2$. In the Whiting mercury cell, the amalgam first formed is made to react with water in a separate chamber, to form also caustic and hydrogen. The several cells are so connected that the current passes from the cathode of one cell to the anode of the next; the path of the current then lies through the metallic bar to the anode, through the liquid to the cathode, through metallic connection to the next anode, and so on to the last cathode, which is connected to the terminal at the generator. In passing through the metal, the current causes no change; in passing through the brine, a decomposition of the salt into chlorine and sodium takes place. Caustic gradually accumulates near the cathode; in order to prevent its free diffusion toward the anode, a wall may be placed in the cell forming two compartments. Diffusion of caustic to the anode would result in the formation of sodium hypochlorite, thus

[5] It would be more correct to say that electrons enter at the cathode, and leave at the anode, but the general custom should be observed.

reducing the yield. This wall allows slow passage of the solution and free passage of the sodium ions; by maintaining the level in the anode chamber higher than in the cathode chamber, the hydrostatic flow of liquor is toward the cathode, nullifying the diffusion tendency of the NaOH toward the anode. The permeable wall is usually asbestos paper or cloth suitably coated and is called the diaphragm.

THE PURIFICATION OF THE SALT SOLUTION

The salt may be in the form of a natural brine, an artificial brine, or rock salt. The purification of the latter includes such steps as may be required for the brines. The salt is shoveled from the box car into an underground hopper feeding an inclined belt elevator or bucket elevator by means of which it is raised to the dissolving tank. This is kept filled, and warm water is pumped in at the base and allowed to overflow at the top; during its passage through the salt it becomes saturated. Instead of a wooden tank, a concrete tower (short) may be used. The brine is collected in the treating tank, where sodium carbonate and bicarbonate are added in amounts just sufficient to precipitate the calcium and magnesium salts. After settling to remove the coarse suspended particles, the cloudy liquor is decanted periodically into a series of large, wooden settling tanks which act at the same time as storage. The tanks are in series, and the brine overflows very slowly from one to the next, so that they function as catch basins. The solution passing out from the last basin is almost clear; it is filter pressed, but the content of solid is so low that the press need be opened but once a week or so. Instead of filter pressing, the brine may be filtered through a sand bed. The filtered salt solution, containing about 25 per cent NaCl, is elevated to a tank above the cells and fed through a constant level boot to a 3-inch pipe with side branch for each cell. The method of regulating the amount fed to the cell varies considerably; one of the simpler schemes is to insert a horizontal plate with small orifice in the vertical branch leading to the anode compartment, with a glass sleeve immediately below the orifice plate to permit observation of flow. The size of the orifice determines the rate of flow.

THE DIAPHRAGM CELLS

All diaphragm cells embody the principle of enclosing the anode compartment by a diaphragm, as originally proposed by C. P. Townsend; they are all therefore referred to as Townsend cells, but the modified constructions of the later cells have been of the greatest importance; furthermore, they differ from each other radically. It is chiefly for convenience that they are grouped together under the same name. Of these modified Townsend cells, a sub-group would be formed by the Townsend-Baekeland [6] and Hooker cells, which are evidently related.

[6] "The new electrolytic alkali works at Niagara Falls," Leo Baekeland, *Electrochemical and Metallurgical Industry*, **5**, 209 (1907). *Also* **7**, 313 (1909), by the same author.

Both have liquor in the cathode compartment, the kerosene in the Town-send-Baekeland cell being replaced by caustic liquor, with a residual salt content, in the Hooker cell. It seems certain that no cell remains in commercial operation with kerosene in the cathode compartment, so that the Hooker cell may be taken as typical of the diaphragm cells which have liquor in the cathode compartment.

The Hooker Cell. The Hooker cell avoids the reworking of the chlorine-laden anode liquor, necessary in the Baekeland cell, by dispensing with the kerosene, allowing instead the partly causticized liquor to accumulate in the cathode compartment. The brine is fed to the anode compartment, but no liquor is drawn from it; instead, liquor is drawn from the cathode compartment. The rate of feed to the anode compartment and the withdrawal from the cathode compartment are equal. The level in the anode compartment is higher than in the cathode chamber. The flow of liquor toward the cathode is strong enough to prevent diffusion of the caustic to the anode.

The Hooker cell, like the Townsend-Baekeland, is a rectangular narrow box, as indicated in Figures 30 and 31. The 4500-ampere unit would
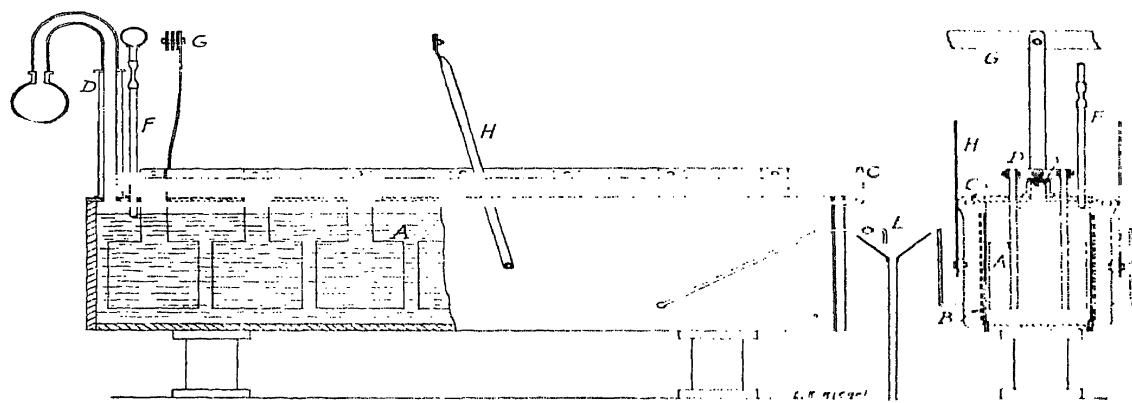
FIGURE 30.—Side view and vertical cross-section through Townsend cell. A, graphite anodes; B, perforated cathode with diaphragm; C, outlet for hydrogen; D, chlorine outlet; E, discharge for caustic liquor; F, brine feed; G, current entering anode; H, current leaving cathode. The level of the caustic liquor in the cathode compartment is lower than the level in the anode compartment.

be about 14 feet long, 3 feet high, and 18 inches in thickness. Each 14 by 3 feet side piece is of cast-iron, forming a narrow vertical chamber just behind the perforated cathode carrying the untreated asbestos paper diaphragm. The base and the two narrow sides are of reinforced concrete. Each cell has for anodes two rows of 9 graphite slabs, each row facing one of the diaphragms carried by the cathode plate at a distance of 1 centimeter. If 60 such cells are united in a bank of cells, a current of 4000 to 4500 amperes would be sent through them (passing from the

cathode of one to the anode of the next; *see* Fig. 31), at 300 volts, each cell requiring a little less than 5 volts. To indicate the capacity of such a bank, its output may be estimated at 10 tons of caustic per day, hence per cell about 330 pounds (98 per cent NaOH).[7] Two or four such banks of cells are placed together in one cell house. The Hooker cell works with high current densities,[8] 100 amperes per square foot of cathode surface;

FIGURE 31.—End view of two Townsend cells showing the electrical connections; 1, cathodes in cell *A* connected to 2, anodes in cell *B*; 3, cathodes in cell *B* connected to anodes in cell *C*, not shown.
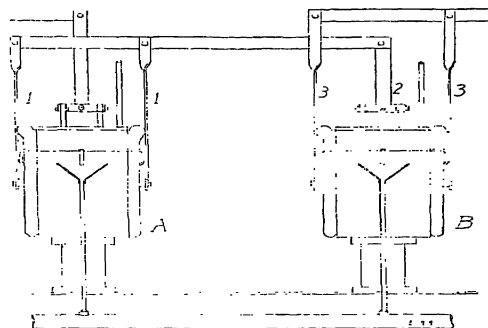
its cathodic current efficiency is 96 to 97 per cent. The temperature of the cell liquor is 60° C. (140° F.).[9] The Hooker cell is one of the largest (in amperes) in operation and has been extremely successful.

The Hooker "S" Type Cell. The most advanced type of diaphragm cell is the "S" cell, with square cross section;[9a] it consists of a concrete top piece, a concrete bottom (set on short legs), and a central steel frame
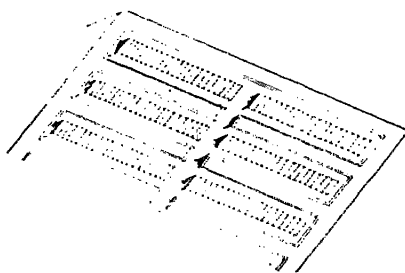
FIGURE 32.—Arrangement of graphite anode blocks and cathode fingers in "S" cell; much simplified.

which carries the multimembered cathode. The cell is proportioned to have minimum (outer) surface to volume ratio, in order to diminish the radiation loss. It is heavily lagged, also to conserve heat. The cell is closely packed with cathode and anode branches, with only a 4-inch central free passage, for anolyte circulation. The cathode is of the finger type,

[7] "Description and views of the Townsend cells and the Niagara Falls plant of the Hooker Electrochemical Company," A. H. Hooker, *Trans. Am. Inst. Chem Eng.*, 13, I, 55-60 (1920).

[8] The current density means the current in amperes per unit surface. An increase in current density requires an increase in voltage.

[9] The higher the temperature, the less the resistance; higher than 90° C. is avoided because of the greater action of the products on the cell walls; 60 to 70° C. is the general

[9a] U. S. Patent 1,866,065, with six sketches.

the fingers reaching in from the sides; they are made up of crimped steel wire covered with asbestos forming diaphragm.[9b] The anode is made up of graphite slabs, set in a bitumen-covered lead base plate, which receives the current; the slabs reach up from below between the fingers of the cathode, so that every vertical face of the cathode is close to a similar graphite surface. A single broad-faced connection at the cathode of one cell carries the current a short distance to the single post feeding
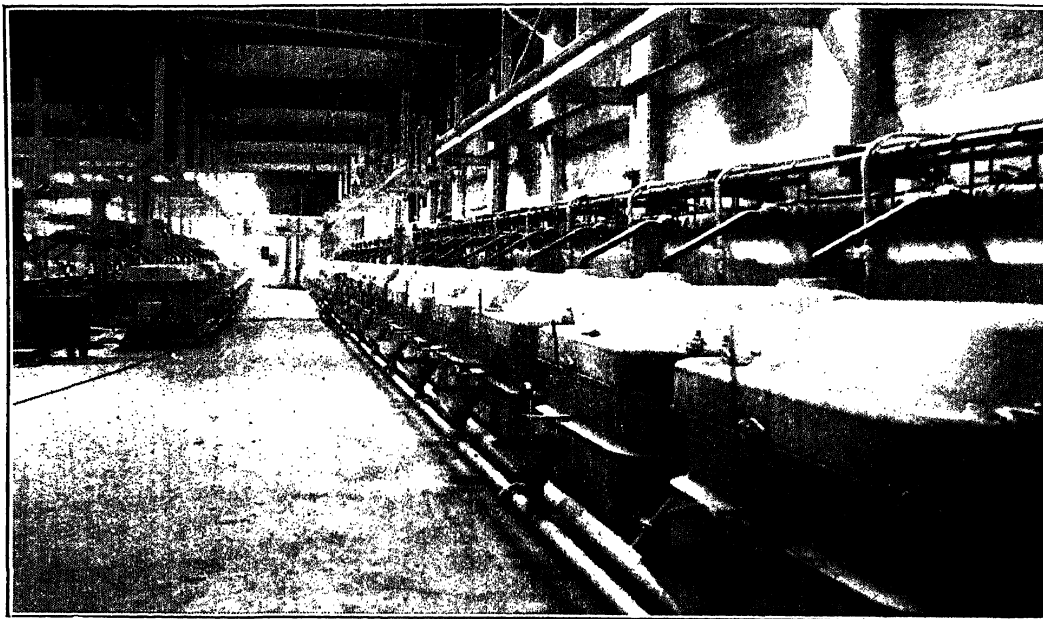

FIGURE 33.—View of a cell room with the new type "S" cell, an improved diaphragm cell, of the Hooker Electrochemical Company. (By permission.) To left of center, note the large bus-bar connection to lower part of cell, and the ½-inch brine delivery line running at an angle to top of cell. Upper right, the large pipe line is for chlorine, the uppermost one, for hydrogen. Note also the different angles of caustic discharge pipes, and the small traveling crane, with free access to the tops of cells.

the anode of the next cell. The cell operates at a higher temperature than its predecessors, at 85° C. [185° F.], which permits the use of a lower voltage; the heat need not come from converted electrical energy; it is merely saved, and transferred from the outgoing products to the incoming brine, both by means of double-walled pipe coils laid in the cell wall, and by interchangers outside of it.[9c] The voltage is better than 3.4 per cell (65 per cent voltage efficiency). The ampere efficiency is very high, for at the increased temperature, less chlorine is dissolved, only a trace of chlorate forms (for example, 97 per cent a-e)).

[9b] U. S. Patents 1,862,244, 1,865,152.
[9c] U. S. Patent 1,862,245.

The cell has other features. Its construction allows the vertical removal of upper section, and of the cathode section; hence the cells may be placed close to each other, an economy in floor space. The horizontal entry of the brine starts the circulation of the anolyte, in order to relieve the working surfaces of the depleted layers of brine. The cell may be as large as needed to take a 10,000-ampere current; 7000 amperes has been the usual size.

Nelson Cell. In the Nelson cell, as also in the Allen-Moore, Vorce, and several other cells, the cathode compartment is empty of liquor; the caustic solution, with residual salt, runs down the diaphragm and collects at the base. In the Nelson cell,[10] steam is sent into the cathode space to maintain the temperature near 65° C. (149° F.). The form of the cell is again a narrow rectangular box set up as the Hooker cell is; the Allen-Moore has a similar outside appearance. There is only one row of suspended graphite anodes, and the usual size unit receives 1000 amperes; the current density is 50 amperes per square foot, half of that in the Hooker cell. The voltage is lower, averaging 3.7 volts. Among other advantages, this cell produces a very pure chlorine; for this reason it was chosen for the installation at Edgewood arsenal during the war.[11] Three thousand and five hundred Nelson cells furnished 100 tons of chlorine per 24 hours; the anodic ampere efficiency (for chlorine) was 90 per cent; the caustic liquor was maintained 10 to 12 per cent NaOH and 14 to 16 per cent NaCl.

Allen-Moore Cell. The Allen-Moore cell [12] has usually 1200 ampere units, working with a voltage of 3.6; the cathodic current efficiency is maintained 95 per cent over extended periods. The caustic liquor contains 8 to 10 per cent NaOH and about 12 per cent NaCl. The cell is constructed of concrete and cast-iron sides, and has in general the shape of a narrow rectangular box. The basic principle of the unsubmerged cathode, that is, of using an empty cathode compartment, was first proposed by the designers of the Allen-Moore cell.[13]

The cell described by L. D. Vorce [14] is cylindrical, and is said to furnish more caustic per square foot of floor space than any other cell. Another cylindrical cell used in Canada, and by the United Alkali Company of Great Britain, is the Gibbs cell,[15] patented in 1907.[16] The units are of 1000-ampere capacity, requiring 3.6 volts; the floor space occupied is small. The Gibbs cell [17] and the Vorce cell have an empty cathode compartment as the Allen-Moore and Nelson cells also have.

The Hargreaves-Bird cell produces sodium carbonate solution. The

[10] *Trans. Am. Electrochem. Soc.*, **35**, 239 (1919), or U. S. Patents 1,149,210 (1915) and 1,149,211.
[11] "The U. S. Government chlorine-caustic soda plant at Edgewood arsenal, Edgewood, Md.," Samuel M. Green, *Chem. Met. Eng.*, **21**, 17 (1919).
[12] "The Allen-Moore cell in the pulp and paper mill," F. H. Mitchell, *Chem. Met. Eng.*, **21**, 370 (1919).
[13] *Trans Am. Inst. Chem. Eng.*, **13**, I, 11 (1920).
[14] *Trans. Am. Inst. Chem. Eng.*, **13**, I, 47 (1920), and U. S. Patent 1,286,844.
[15] *Ind. Eng. Chem.*, **16**, 1056 (1924).
[16] Brit. Patent 28,147, also U. S. Patent 874,064.
[17] In its original form, the Gibbs cell had caustic liquor in its cathode compartment.

caustic soda primarily formed is changed to the carbonate at once by carbon dioxide and steam injected into the cathode compartment. The Griesheim cell has magnetite anodes, and solid salt is fed into the anode liquor.

CONCENTRATION OF THE CAUSTIC LIQUOR

The liquor flowing off from the cathode compartment contains both caustic and salt, for the diaphragm cells just discussed. The solution contains about 12 per cent NaOH and 12 per cent NaCl. It is concentrated in a double-effect evaporator,[18] for example, and each boiling pan may have its own separator in which the salt is collected as fast as it separates from solution, so that the heating surface in the pan may always be swept by liquor. When a batch of cell liquor has been concentrated to 50 per cent NaOH only 1 per cent salt remains in the solution. The suspension from pan and separator is pumped to a settler with monel wire over a conical base; the salt settles on the wire, the caustic liquor collects in the cone. The liquor passes to cooling tanks where any salt in suspension is carefully removed by settling. The 50 per cent liquor next reaches the cast-iron pots heated by coal or oil fire, where all the water is evaporated; the liquid anhydrous caustic, with perhaps 2 per cent NaCl, is removed from the pots by a centrifugal pump lowered from a crane.[19] The liquid caustic is pumped to thin steel drums on low trucks; after cooling, the mass is solid. The weight of a caustic drum is generally 700 pounds net. Caustic soda is also marketed in crushed form, particularly for household uses; in flakes; and in the form of 50 per cent liquor, which is cheaper since the final evaporation in the caustic pot need not be performed.

The salt in the settlers is washed a number of times by liquors of decreasing caustic content; it is made up to a soft mush and pumped to the dissolver, re-entering the system with the raw salt solution.

In order to produce an absolutely iron-free caustic, some plants are now substituting for the pots continuous evaporators constructed of nickel.

THE MERCURY CELL

Castner Cell. In the Castner cell, the sodium formed at the cathode is dissolved in mercury to be changed to caustic in a subsequent operation. In the original form of the Castner cell [20] the removal of the amalgam to the denuding chamber was by tilting, about once a minute, through a distance of one-half inch. Such a cell consists of a low slate box with three chambers; each of the two decomposing compartments have a graphite anode and mercury cathode; the chamber in the middle is the denuding chamber, with an iron cathode suspended over the amalgam layer. The partitions between the chambers reach into grooves which

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[18] Chapter 43.
[19] For an account of the method of evaporation, compare *Ind. Eng. Chem.*, **16**, 1057 (1924).
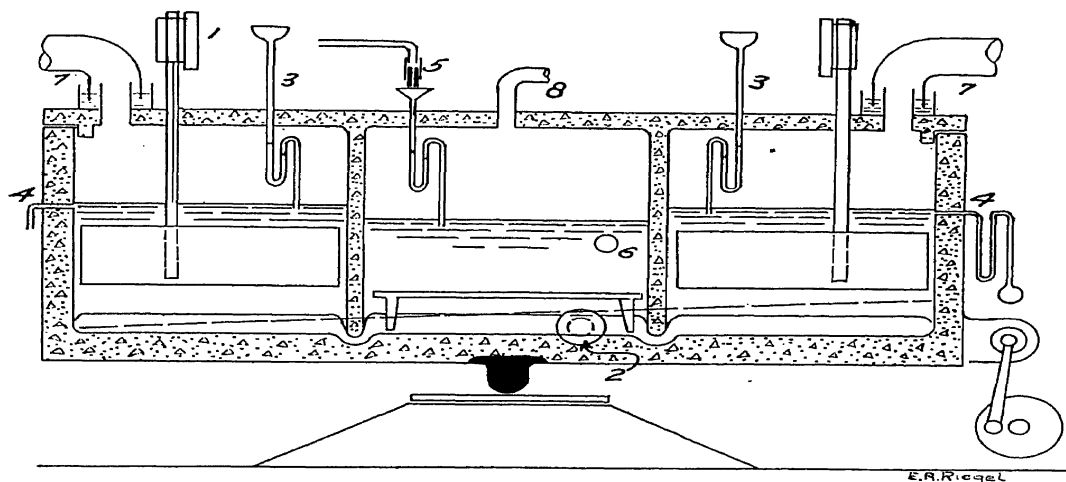[20] *Electrochem. Ind.*, **1**, 11 (1902).

FIGURE 34.—Cross-section through the Castner cell, original type, showing the three longitudinal compartments, also shown in the next sketch. 1, anode; 2, cathode; 3, entry for brine; 4, exit for depleted brine; 5, water entry; 6, exit for caustic solution; 7, outlet for chlorine; 8, hydrogen escape. Note pivoting rib. When the cell tips to the right, the level of the mercury with respect to the cell walls is as shown by the dotted line, 4 to 4, 4 feet.

are sealed with mercury but permit the amalgam to pass freely. The current enters at the anodes and leaves at the iron cathode. Brine is fed to the two decomposing compartments; water enters the denuding chamber while a solution of caustic, free from salt, leaves it; outlets for chlorine from the anode compartments and hydrogen from the denuding com-
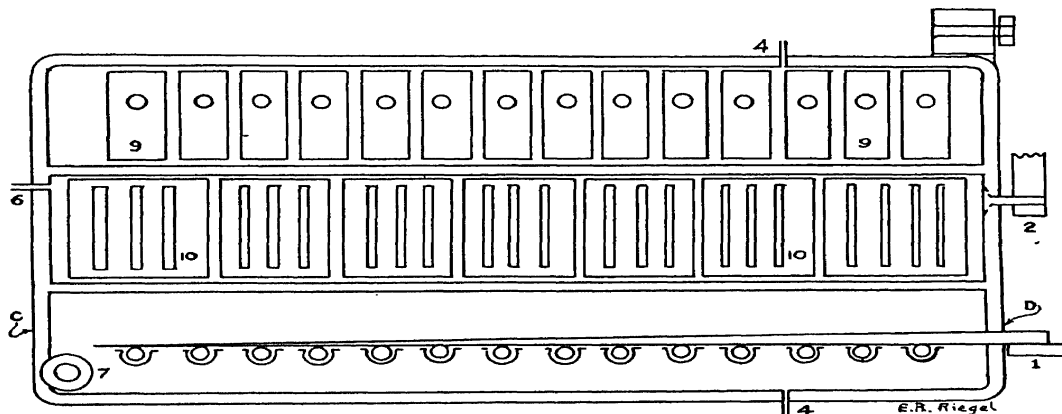
FIGURE 35.—Top view of the Castner cell, original type, with the cover removed from two of the chambers; the third chamber has its cover on, and shows the anode fingers coming to the bus bar. The numerals have the same meaning as in the previous sketch; in addition, 9, stands for the anode slabs; 10, the iron grids dipping in the mercury. C to D, 8 feet.

partment are provided. The units are fairly large, over 1000 amperes; the voltage is about 4; a liquor containing as high as 25 per cent NaOH is obtained. The concentration of the caustic is greatly simplified by the absence of salt.

Whiting Cell. The operation of a mercury cell appears simple and free from difficulties; but in reality very few plants have succeeded in operating the unmodified Castner cell. The chief difficulty according to Whiting is the incomplete removal of the amalgam from the decomposing compartment. In the modified cell[21] the mercury is stationary during electrolysis; after 2 minutes, a valve opens which permits the amalgam to flow into a chamber below it, where it is denuded; the free mercury is lifted by a bucket wheel to a reservoir-trough just above the decomposing chambers, and is run in at 2-minute intervals. Five chambers make up one cell, so that the operation of the cell as a whole is continuous. A cell of five sections is 6 feet square, takes 1200 amperes at 4 volts per cell; the cathodic current efficiency is 90 to 95 per cent.

The merit of the mercury cells is that they produce a caustic free from chloride.

The Bell-Jar Type Cell

Billiter Cell. In the Billiter cell,[22] the graphite anode is suspended in a bell-like housing, from which the chlorine is drawn off; the cathode consists of a number of iron rods slightly inclined from the horizontal; each rod is surrounded by a tight asbestos tube. At the edge of the jar, the rods and tubes rise upward; as the hydrogen is evolved along the rods, it travels upward, carrying with it the caustic liquor which is

TABLE 8.—*Estimated Distribution of Caustic Soda Sales in the United States (in short tons).**

Consulting Industry	1935	1936
Rayon, cellulose film	160,000	174,000
Chemicals	118,000	130,000
Soap	96,000	104,000
Petroleum refining	87,000	95,000
Exports	69,500	72,000
Pulp and paper	40,000	46,000
Lye	38,000	46,000
Textiles	34,000	43,000
Rubber reclaiming	11,000	13,000
Vegetable oils	9,000	10,000
Miscellaneous	56,500	63,000
	719,000	796,000

* *Chem. Met. Eng.*, **44**, 77 (1937).

delivered to a small receiving chamber in each cell, from which it is sent to the evaporators. The brine entry into the bell is such that the flow is toward the cathode, and as the caustic is carried out as fast as formed, it does not interfere with the passage of the current.

[21] *Trans. Am. Electrochem. Eng.*, **17**, 327 (1910), also U. S. Patents 951,228-9.
[22] British Patent 11,693 (1910).

The estimated distribution of caustic soda sold in the open market is given in Table 8.

By-Products of Electrolytic Caustic Soda

Hydrogen from the cathode chamber and chlorine from the anode chamber are the by-products of electrolytic caustic soda. The hydrogen is generally wasted, except that in some plants chlorine is burned in an excess of hydrogen to give a very pure hydrogen chloride which dissolved in water gives hydrochloric acid. It is likely that in the future, all of the hydrogen will be utilized. The chlorine is the more important by-product of the two; it is produced at the rate of some 230,000 tons a year.

Liquid Chlorine. Chlorine is easily liquefied to a brown liquid; this circumstance has extended its usefulness considerably over that which the gas possesses. At 0° C. (32° F.), a pressure slightly over 39 pounds will cause liquefaction; at −20° C. (−4° F.), slightly over 12 pounds are needed; at −33.5° C. (−28.5° F.), only a little over atmospheric pressure is required. A temperature of −20° C. may be obtained with an ammonia refrigerating system, brine or gas, while −40° C. (−40° F.) is obtained by a carbon dioxide system (Chapter 12).

The chlorine gas leaves the anode compartment warm and moist; under gentle suction it passes along a 3-inch stoneware line to a stoneware or quartz S-bend cooling system.[23] It next enters a stone box filled with scrap iron; ferric chloride forms which is exceedingly hygroscopic and removes much of the water in form of a strong ferric chloride solution.[24] More frequent than the ferric chloride box is a series of two short towers with large disks made up of coils through which water, the incoming brine, or refrigerated brine circulates; the condensate is run to the sewer. The partly dried gas may then be circulated in a battery of Cellarius vessels through which 66° Bé. sulfuric acid flows in the opposite direction (counter-current principle). It next reaches a Nash[25] turbo-blower, whose multibladed impeller works in sulfuric acid held in an elliptical casing. For each revolution there are two compressions and two expansions of the working fluid, caused by the shape of the casing; the alternate compression and expansion move the gas. A pressure of 15 pounds may be obtained. The compressed gas is cooled in double-walled tubes, through the inner passage of which liquid carbon dioxide is expanding. The chlorine liquefies at a rapid rate, and is led to a steel storage tank. Any of the less compressible gases present as impurities, such as carbon dioxide, monoxide, and hydrogen, are vented from the storage tank to bleach chambers.

The liquid chlorine is shipped in 50- and 100-pound steel cylinders,

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[23] *Chem. Met. Eng.*, **21,** 17 (1919).
[24] U. S. Patent 1,359,047.
[25] Nash Engineering Company, South Norwalk, Conn.; sketch in Chapter 41.

in single tank car units of 15 or 30 tons, and in 1-ton steel containers of which 15 are placed on a flat car.[26]

The 1-ton unit is very convenient for making the bleach at the pulp or other mill, because the required quantity of milk of lime may be prepared and all the chlorine in the cylinder allowed to pass in without danger of wasting any. There is formed calcium hypochlorite $Ca(OCl)_2$ and $CaCl_2$. All containers have one or two internal pipes, so that either the gas may be drawn, or the liquid. If the gas is drawn, heat must be supplied to make up for the heat of vaporization, or else the process is very slow. It is most convenient and simple to use the liquid, mixing it directly with the milk of lime in a small mixing chamber [27]; in that way the process of vaporization uses a part of the heat of reaction of chlorine on lime. In the summer time, this is important in keeping the temperature of the mixture below 40° C.; above that point the calcium hypochlorite is unstable.[28]

For the chlorination of municipal water supplies, and for any other chlorination away from the manufacturing plant, chlorine in the liquid form is preferred.

In 1935, there were produced 319,303 tons of chlorine, a great increase over the production of the previous year, 217,089 tons, which itself was better than the 180,870 tons of 1931. The 1935 value was $38.41 a ton; the 1933 selling price was $36.02 a ton. These figures are exclusive of chlorine made and consumed by the wood-pulp industry.[28a]

Distribution of liquid chlorine for an average year follows:

Pulp and paper .... 65%   Sanitation 10%
Textile .... 20%   Miscellaneous 5%

Gaseous Chlorine and Bleach. Chlorine gas at the generating plant is used, without compression to the liquid, to make "bleach," and for the chlorination of organic substances such as benzene, toluene, pentane, and others.

Bleaching powder is the product of the interaction of chlorine gas on hydrated lime: $Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O$. The chloride of lime so formed, when dissolved in water, gives equal molecular parts of calcium chloride, which as far as bleaching is concerned, is useless, and calcium hypochlorite, which retains the total bleaching power of the original material

$$2CaOCl_2 \text{ dissolved} = CaCl_2 + Ca(OCl)_2.$$

Chloride of lime or "bleach" must not be confused with calcium hypochlorite.

[26] Through a recent decision of the Interstate Commerce Commission the containers are considered as part of the car, and no freight is paid on them. See I. C. C. Docket 13895, 85 I. C. C. 728 (1924); Invest. & Susp. Docket 2456, 104 I. C. C. 196 (Nov. 9, 1925).

[27] U. S. Patent 1,481,106, to James H. MacMahon, assigned to the Mathieson Alkali Works (Inc.), of New York; the time required for the absorption of 1 ton of chlorine is 3 hours.

[28] The bleaching solution used in the pulp and paper mills is 6° Bé. and contains 30 grams of available chlorine to the liter.

[28a] Bureau of the Census.

The chlorine absorption is performed either in a series of low-ceiling brick chambers, or in patent shelf absorbers which require little space. In either case the counter-current principle is applied, the fresh gas meeting the richest bleach; the lean gas, the new hydrated lime. The bleach so prepared has been displaced to a certain considerable degree by (1) liquid chlorine, in mills and factories, (2) by calcium hypochlorite $Ca(OCl)_2$, a stable material of high test, while ordinary bleach spoils after several months, and has a low test (35 per cent available chlorine). Available chlorine means chlorine evolved on addition of acid; 35 per cent available chlorine is a material which has the effectiveness of 35 parts of liquid chlorine. Pure calcium hypochlorite, by the laboratory test applied to all bleaching agents, rates 100 per cent available chlorine.[29]

In 1929, the production of bleach was still 93,116 tons; in 1923, it had been 146,975 tons.

High Test Hypochlorite [H. T. H.]. Calcium hypochlorite $Ca(OCl)_2$, essentially free from any other material, in the crystal form, is a stable material and efforts to produce it in bulk have been earnest and successful.

One method for its manufacture is the chlorination of a lime slurry followed by the salting out of calcium hypochlorite by means of common salt (NaCl).[30] No organic solvent [31] requiring later recovery is needed. The product may be made essentially 100 per cent $Ca(OCl)_2$, but an additional operation is then required, so that the material actually marketed is 75 per cent $Ca(OCl)_2$. It is therefore twice as strong as ordinary bleach, also it does not spoil on standing, it is not hygroscopic, and made up with water the solution is practically clear.

The latest and most successful method for making high test hypochlorite (H. T. H.) is the formation of the newly-discovered [32] triple salt $Ca(OCl)_2 . NaOCl . NaCl . 12H_2O$ and its subsequent reaction with calcium chloride. The triple salt is made as follows: 40 parts NaOH, 37 parts $Ca(OH)_2$ and 100 parts water are chlorinated at a temperature below 16° C. (60.8° F.), such as 10° C. (50° F.). This reaction (a) is: $4NaOH + Ca(OH)_2 + 3Cl_2 + 9H_2O \rightarrow Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O + 2NaCl$. The comparatively large hexagonal crystals, the triple salt, separate, and are centrifuged. In the meantime a special calcium chloride

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[29] The test for available chlorine in bleaching powder consists of acidifying in the presence of potassium iodide. The iodine liberated is titrated. It may be liberated by Cl, but also by oxygen.

Calcium hypochlorite contains 99.7 per cent available chlorine, yet only 50 per cent total chlorine; it is evident that a change in the method of designating the strength of bleaches is desirable. The most logical way would be to state the content of calcium hypochlorite, and this would also be the easiest for it happens that numerically, the present "available chlorine" is almost the same as the calcium hypochlorite content. The chlorine equivalent for calcium hypochlorite is shown by the reactions:

$$Ca(OCl)_2 + H_2SO_4 = CaSO_4 + 2HOCl$$
$$2HOCl + 4HI = 2H_2O + 4I + 2HCl, \text{ and } 4I \text{ are equivalent to } 4Cl.$$
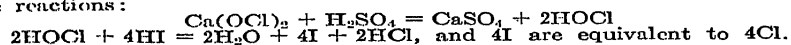
Bleaching was explained formerly as oxidation; today it would be said to be the taking of electrons. A substance which yields fragments (ions) which take up electrons is an oxidizing agent. Measured in that way, oxygen as well as chlorine is a bleaching agent, a fact already well known in an empirical way.

[30] U. S. Patent 1,754,473 (1930).

[31] U. S. Patents 1,481,039-40.

[32] U. S. Patent 1,787,048, to Robert MacMullin and Maurice Taylor; *see also* U. S. Patents 1,787,080, 1,754,474, 1,754,475.

is prepared by chlorinating a milk of lime, in these proportions: 74 parts $Ca(OH)_2$, 213 parts water, 71 parts chlorine; the temperature is held at 25° C. (77° F.): (b) $2Ca(OH)_2 + Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$. Next, this solution is cooled to 10° C. (50° F.), the centrifuged crystals are added in the proportion required by the reaction (c) $2NaOCl + CaCl_2 \rightarrow 2NaCl + Ca(OCl)_2$, and the suspension is agitated with paddles. On warming to 16° C. (60.8° F.), reaction (c) takes place and the whole sets to a rigid mass. The triple salt $Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12H_2O$ becomes $1\frac{1}{2}Ca(OCl)_2 \cdot 2H_2O$, the dihydrate, $2NaCl$ and water. After drying in the vacuum, a material testing 65 to 70 per cent $Ca(OCl)_2$ results. Such calcium hypochlorite as accompanied the calcium chloride is just that much more product. The NaCl content from (c) is not removed.

OTHER PATENTS

U. S. Patent 1,236,978 on a method for making high test calcium hypochlorite; 1,862,244, on cell construction; 1,862,245, on heat recovery in electrolysis; 1,996,769, manufacture of stable sodium hypochlorite; 2,040,717, 2,028,898, 2,030,694, purifying caustic solutions; 2,031,844, 1,922,591, manufacture of caustic soda; 1,609,757-8, process and apparatus for preparing liquid bleach.

PROBLEMS

1. An 18 per cent $NaCO_3$ solution is made to react with a 28 per cent $Ca(OH)_2$ slurry. (a) Assuming the reaction to be complete, what will be the concentration of the resulting decanted caustic soda solution? (b) Consult the curve for conversion against concentration of sodium carbonate solution, and find the figure for 18 per cent Na_2CO_3; using this conversion figure, what will be the concentration of the caustic soda solution? For exact results, the weight of the non-converted Na_2CO_3 present in the caustic soda liquor must be computed and included in the solids which the liquor contains.

2. A batch of soda ash solution containing 19 per cent Na_2CO_3 is treated with the proper amount [use (a) the theoretical, (b) the amount required by a 94 per cent conversion figure] of a milk of lime containing a certain amount of water. How much water must the milk of lime contain, if the resulting caustic liquor is to be 11 per cent NaOH? Find the answer for (a) and (b).

3. A plant causticizes 149 tons of soda ash (98.5 per cent Na_2CO_3) every day. The lime used is 94 per cent CaO. Allowing a 4.5 per cent excess of lime, and assuming that none is recovered, how many tons of lime will be required? What is the production of 50 per cent NaOH liquor, if the yield based on soda ash is 94 per cent?

4. A battery of 60 Nelson cells produces per day 10 tons of chlorine, at an anodic current efficiency of 93 per cent. The cathodic current efficiency is the same. How much caustic soda is produced at the cell? What is the current in ampere hours which passes through the cell if 1 ampere hour is required for 0.00329 pound of NaOH at 100 per cent current efficiency?

5. A plant has 18 tanks with capacity of 40,000 gallons each. The salt solution contained therein is 25 per cent NaCl, and has a specific gravity of 1.200. The plant produces per day 32 tons 850 pounds of 100 per cent NaOH, at 95 per cent yield. What is the storage capacity of the tanks expressed in days? In reality, the final product is 98 per cent NaOH for the diaphragm cell plants, and the remaining 2 per cent is salt (NaCl) and a small amount of carbonate; for the sake of simplicity, the purity is given as 100 per cent NaOH in this problem. Answer: 18 days.

6. The liquor from the electrolytic diaphragm cell contains 12 per cent NaOH and 12 per cent NaCl. For a production of 10 tons of solid caustic per day, how much salt will precipitate in the evaporator, if 2 per cent remains in the caustic? What decomposition efficiency does the cell liquor represent?

7. Verify the decomposition voltage for salt in solution to produce caustic and chlorine, given as 2.25 in the text. The heat of formation of NaCl is 96,400 gram calories; that of water, 68,370 gram calories, and that of caustic in solution, 112,700 gram calories. Compare Problem 4, Chapter 18.

8. It is desired to manufacture 75 tons of calcium hypochlorite testing 75 per cent "available chlorine" by the salting out method, the first method given under H. T. H. Find out how much lime will have to be used, how much chlorine, and how much calcium chloride in solution will be discarded. The relation may be assumed to be the theoretical ones.

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Atmospheric nitrogen is available in inexhaustible quantities. To convert this vast store of nitrogen into a raw material for the manufacture of indispensable fertilizers and peace-time as well as war-time explosives has been one of the major tasks of the chemist. He has discharged it brilliantly. Of the total compounds made or extracted for their nitrogen values, 75 per cent are "chemical nitrogen," or "air nitrogen" compounds.

Chapter 6

Synthetic Nitrogen Products—The Fixation of Atmospheric Nitrogen—Direct Ammonia, Cyanamide, Nitric Acid from Ammonia by Contact Catalysis

As long ago as **1780** Cavendish caused the combination of the nitrogen and oxygen in the air by means of an electric spark. The first practical large-scale manufacture of a nitrogen compound from atmospheric nitrogen was that of Birkeland and Eyde, at Nottoden, Norway, early in this century. In this process air is passed at a rapid rate through an arc spread out to form a flame. A previous attempt by Bradley and Lovejoy at Niagara Falls in 1902, using the arc method, had failed because the arc flame area was too small and because the gases were not removed from the reaction chamber fast enough. The Norwegian process benefited from the demonstrated faults in this installation.

The manufacture of synthetic ammonia was tried a little later, and succeeded first in the Haber process, in which a mixture of nitrogen and hydrogen is passed at moderately high temperature and under pressure over a contact catalyst, which causes a partial conversion of the elemental gases into ammonia. Several modifications of the process have been developed for making ammonia from the elements; they have been so successful that this process is now more important than all other synthetic processes combined. Ammonia salts are valuable fertilizers; moreover, if nitric acid is called for, ammonia may be oxidized with atmospheric air by the aid of a contact catalyst, so that the synthetic ammonia process may also produce from atmospheric nitrogen, in an indirect way, what the arc process furnishes directly.

An entirely different process for the fixation of atmospheric nitrogen is the calcium cyanamide process, which depends upon the fact that metallic carbides, particularly calcium carbide, readily absorb nitrogen gas to form the solid cyanamide. This substance as such is a fertilizer. By a further treatment it may be transformed into cyanide; by another into ammonia, but this ammonia is dearer than direct synthetic ammonia. The process was developed by Frank and Caro in Germany, in **1895-97**, and has been introduced in many countries since that time, among others in the United States and Canada

Another process for binding the nitrogen gas of the air in the form of a chemical compound easily transported, which is what "fixation of

atmospheric nitrogen" means, is the Bucher process which produces cyanides, ferrocyanides, or hydrocyanic acid without using a carbide. It is of no commercial importance at present.

Finally, nitrogen may be passed over metals at suitable temperatures to form nitrides which on treatment with steam yield ammonia. The best known process which embodies this principle is the Serpek process, manufacturing aluminum nitride; it has been introduced in France but not in America.

The various processes for the fixation of atmospheric nitrogen and their principles may be grouped together as follows:
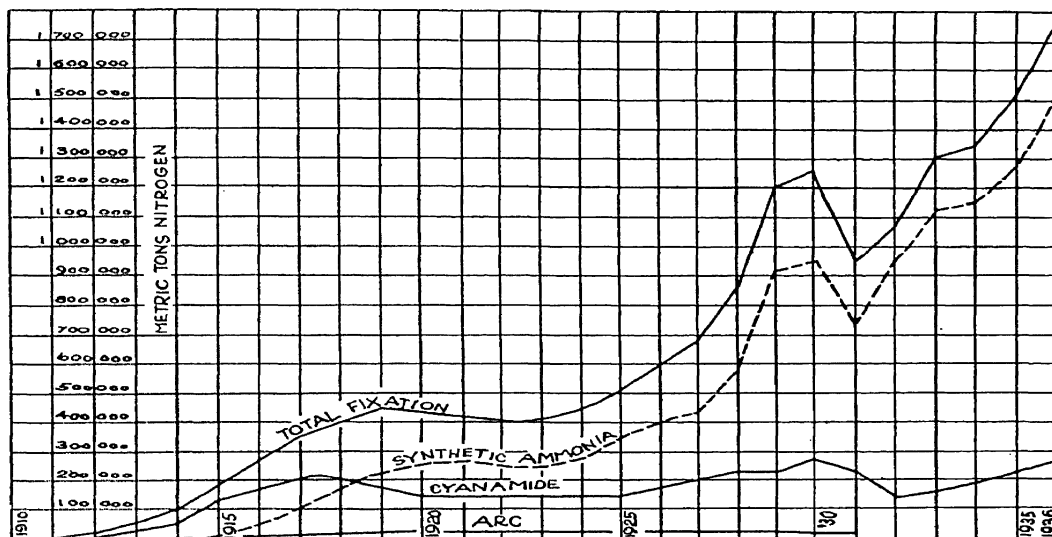
FIGURE 36.—The growth of atmospheric nitrogen fixation (based on information from Fertilizer Investigations, Bureau of Chemistry and Soils, Department of Agriculture, Washington, D. C.).

a. The various arc processes in which ordinary air is passed at a rapid rate through a broad or long arc. The products are nitrates, nitrites, or nitric acid. This was the earliest process, but is hardly a factor any more.

b. The direct synthetic ammonia process, requiring nitrogen free from impurities, and pure hydrogen. The two gases mixed sweep over a catalyst while under pressure and at an elevated temperature; the product is ammonia, which may be further combined as a salt, such as the phosphate or the sulfate. By catalytic oxidation, the ammonia may be changed to nitric acid, and this in turn into nitrates. The great expenditure of electrical energy required in a is avoided in b.

c. The cyanamide process, which also requires fairly pure nitrogen, and calcium carbide, itself a product of the electric furnace. The mate-

rial produced is calcium cyanamide. By steaming in autoclaves, ammonia is produced.

d. The cyanide and ferrocyanide processes, in which nitrogen is passed into a vessel containing an alkali and coal mixed and heated.

e. The nitride process, in which nitrogen gas unites with certain metals. The product as such is not used; it is treated with water, yielding ammonia.

The reason why the fixation of atmospheric nitrogen has been a difficult task is that elemental nitrogen is comparatively unreactive. It combines with only a few other elements, and then only under violent means, such as elevated temperatures.

The relative industrial importance of the three most important processes, *a, b,* and *c,* is shown in Figure 36. A glance suffices to tell that the synthetic ammonia process leads.

The capacity for the production of direct synthetic ammonia in the United States, on January 1934, was 341,350 tons (2,000 lbs.) of nitrogen annually, which was 10.6 per cent of total capacity of similar plants for the world. Germany is the leader, with 1,136,080 tons installed capacity.[1]

Table 9 shows the world production for several years of nitrogen compounds in every form, Chile nitrate, by-product ammonia, synthetic ammonia and other nitrogen compounds.

TABLE 9.—*World Production of Nitrogen Compounds, in Metric Tons of Nitrogen.**
(The year is from July 1st of one year to June 30th of the next).

	1935-36	1934-35	1933-34	1932-33
Total world production	2,378,000	2,070,000	1,792,000	1,677,000
Sulfate of ammonia				
by-product	365,000	321,000	307,000	258,000
synthetic	630,000	533,000	535,000	560,000
Cyanamide	270,000	232,000	195,000	168,000
Nitrate of lime	156,000	153,000	107,000	118,000
Other forms of synthetic nitrogen**	720,000	607,000	516,000	462,000
Other forms of by-product nitrogen	45,000	45,000	48,000	40,000
Chilean nitrate	192,000	179,000	84,000	71,000
Total world consumption	2,400,000	2,071,000	1,878,000	1,747,000
Agricultural consumption	2,068,000	1,812,000	1,673,000	1,586,000

For the year 1935-36, the synthetic nitrogen products were 75.1 per cent, the by-product nitrogen compounds 17.3 per cent, and the Chilean nitrate 7.6 per cent of the total world production, based on the nitrogen content.

The world production capacity for synthetic nitrogen is 3,700,000 tons a year.

* From the report of the British Sulphate of Ammonia Federation, Ltd., 1935-36, kindly made available through the U. S. Bureau of Foreign and Domestic Commerce.

** Other forms of synthetic nitrogen mean: anhydrous liquid ammonia, Nitrochalk, Calnitro, urea, sodium nitrate, and others.

THE ELECTRIC ARC PROCESS, USING AIR

The electric arc has been successfully applied to the fixation of atmospheric nitrogen; it was the first method evolved which permitted the fixa- ·

[1] A richer table will be found in "Chemical Nitrogen," **Report 114,** *U. S. Tariff Commission.* (1937), tables 7 and 70. An earlier article is "World nitrogen developments in 1931," Chapin Tyler, *Chem. Met. Eng.,* **39,** 44 (1932).

tion of such nitrogen. The main developments were the Birkeland and Eyde, in Norway; the Schoenherr, in Germany, and the H. and A. Pauling in Austria; in each of these developments, the shape of the arc differs, and also the shape of the furnace. They agree, however, in the nature of the reaction, the union of atmospheric oxygen and nitrogen to form nitrogen oxide, NO, under the influence (chiefly thermal) of the arc; in all three, the reacted air, with 2 per cent NO, must be withdrawn from the reaction zone as rapidly as possible, in order to prevent decomposition. This first oxide is oxidized further and absorbed in water or in lime, to give nitric acid of medium concentration in the first case, or calcium nitrate, a fertilizer, in the second case. Since the advent of synthetic ammonia, these furnaces have lost their importance, and probably only one of them is still operated, and even that is doubtful. One other reason for their failure is the high power requirement; 1 kilowatt year was required for the production of 600 kilos of nitric acid calculated as 100 per cent HNO_3.[2]

The temperature of the flaming arc was estimated as 3200° C. (6000° F.).

The Direct Synthetic Ammonia Process, by Catalysis

If nitrogen and hydrogen are mixed and brought in contact with a substance such as specially prepared porous iron granules, at elevated temperature and under high pressure, they unite to form ammonia; $N_2 + 3H_2 \rightarrow 2NH_3 + 24$ Cal. Even without the contact substances, the two original gases form ammonia in minute amount; this is of extreme importance, for a catalyst can only hasten the reaction which takes place to slight extent without it. That an increase in pressure should favor the formation of ammonia is due to the fact that 4 volumes of the original gases are changed into 2 volumes of the final gas.[3] The tem-

TABLE 10.—*Percentage Ammonia at Equilibrium.**
Ratio $H_2/N_2 = 3$.

Temp. ° C.	Pressure (atm. absolute)						
	1	10	50	100	300	600	1000
200	15.30	50.66	74.38	81.54	89.94	95.37	98.29
300	2.18	14.73	39.41	52.04	70.96	84.21	92.55
350	0.90	7.41	25.23	37.35	59.12	75.62	87.46
400	0.44	3.85	15.27	25.12	47.00	65.20	79.82
500	....	1.21	5.56	10.61	26.44	42.15	57.47
600	....	0.49	2.25	4.52	13.77	23.10	31.43
700	....	....	1.05	2.18	7.28	....	12.87

* Compiled from publications of the Fixed Nitrogen Research Laboratory by Dr. Alfred T. Larson.

perature must only be high enough to allow high activity: beyond a certain value, an increase in the temperature retards the reaction by

[2] "The fixation of atmospheric nitrogen," Joseph Knox, New York, D. Van Nostrand Co., 1914. *See also* first edition of the present book.

[3] This is in conformity with the principle of Le Chatelier, that "if an outside impulse is applied to any system in equilibrium, the system tends to rearrange itself to absorb that impulse." In this case, the gases contract, in obedience to the pressure applied, by changing, to a greater extent, to the less voluminous ammonia.

"Industrial nitrogen compounds and explosives," G. Martin and W. Barbour, Chapter 4, on the cyanamide industry, London, Crosby Lockwood, 1917.

"The world's inorganic nitrogen industry," F. A. Ernst and M. S. Sherman, *Ind. Eng. Chem.*, **19**, 196 (1927), with valuable statistics.

"Commercial oxidation of ammonia to nitric acid," Charles L. Parsons, *Ind. Eng. Chem.*, **11**, 541 (1919), and "Nitric acid from ammonia," by the same author, *Ind. Eng. Chem.*, **19**, 789 (1927), both illustrated.

"Pioneering chemical and fertilizer production in Western Canada," S. D. Kirkpatrick, *Chem. Met. Eng.*, **38**, 626 (1931).

"Unexpected developments in 1932 nitrogen production," Chaplin Tyler, *Chem. Met. Eng.*, **40**, 36 (1933).

"Catalysts for oxidation of ammonia to oxides of nitrogen," S. L. Handforth and J. N. Tilley, *Ind. Eng. Chem.*, **26**, 1287 (1934).

"Chemical Nitrogen, a survey of processes, organization, and international trade, stressing factors essential to tariff consideration," **Report** 114, second series, *United States Tariff Commission* (1937). This report is really a book of 300 pages. (For sale by the Superintendent of Documents, Washington, D. C., 25 cents.)

favoring the decomposition of ammonia. The amount of ammonia expressed in percentage by volume, for different pressures and temperatures, in the presence of a catalyst, is shown below in Table 10.

These values are obtained only if plenty of time is available, more time than can be allowed in a commercial application. A moderate percentage, but one quickly reached, is best suited to a commercial development, and the rapidity depends upon the nature of the catalyst. All of the gases do not react, but that is not necessary to render the reaction of commercial value; if the portion which has reacted is about 5 per cent, it can be removed and the remaining gases used over again. There are several systems which depend upon this principle, the Haber in Germany, the Claude in France, the Casale in Italy, and the American in the United States.[4] The Haber was the first to employ the direct synthetic method, and the others are indebted to it for the demonstration of the feasibility of the process on the commercial scale. The Claude, the Casale, and the American (or F. N. R. L.) systems are, however, independent developments of the general principle common to all four. They differ from the Haber and from each other in the pressure employed, in the method of removing the ammonia formed, and in the preliminary manufacture and purification of the raw gases. Additional processes with characteristic features are the Fauser, and Mont Cenis.

The American system is the contribution of the Fixed Nitrogen Research Laboratory, Department of Agriculture, Washington, D. C. The details of this system have been made public without reservation, including the method of preparing the catalyzer; it will therefore be presented first.

The American System. The method for the preparation of a mixture of 3 volumes of hydrogen and 1 volume of nitrogen differs with the size of the plant as well as with the system operated. In a small-scale installation, for experimental purposes, a simple way is to burn hydrogen from electrolytic cells which decompose water, in an excess of air. The oxygen of the air is fixed as water and this is removed by a cold water condenser; the gas passing out of the condenser will consist of hydrogen excess, mixed with nitrogen. For full-scale installations, a mixed water gas, producer gas, and steam is passed over suitable catalysts; the carbon monoxide reacts with steam to form carbon di-

[4] The most important direct synthetic ammonia plants in the United States* with their capacity (January, 1934), in tons of 2,000 pounds of nitrogen are:

	Process	Hydrogen from	Capacity
Solvay Process Co., Hopewell, Va.	Own	Water gas	200,000
Du Pont & Co., Belle, W. Va.	Claude & Casale	Water gas	100,000
Shell Chemical Co., Pittsburg, Calif.	Mont Cenis	Natural gas	24,000
Mathieson Alkali Co., Niagara Falls	Nitrogen, Engineering Corporation	Electrolytic by-product	4,800
Midland Ammonia Co., Midland, Mich.	American	Electrolytic by-product	4,800
Pennsylvania Salt Co., Wyandotte, Mich.	Mont Cenis	Electrolytic by-product	4,000
Du Pont & Co., R&H, Niagara Falls	American	Electrolytic by-product	3,000

* *U. S. Tariff Commission* **Report 114,** (1937).

oxide and hydrogen. The carbon dioxide is scrubbed out as described more fully under the Haber process. Hydrogen from any source (Chapter 19) and nitrogen from the liquefaction of air may be mixed in the proper proportions and used.

The Purifier. The several steps in the American system are illustrated in the accompanying flow sheet (Fig. 37). The hydrogen was obtained in this case from electrolytic cells, because of their compactness and ease of operation. A blower feeds the hydrogen to the burner; a cold water condenser liquefies the water formed and a trap removes it. A compressor (4-stage) delivers it at a pressure of 300 atmospheres to the purifier, which is really a low-efficiency converter. (See Fig. 38.)
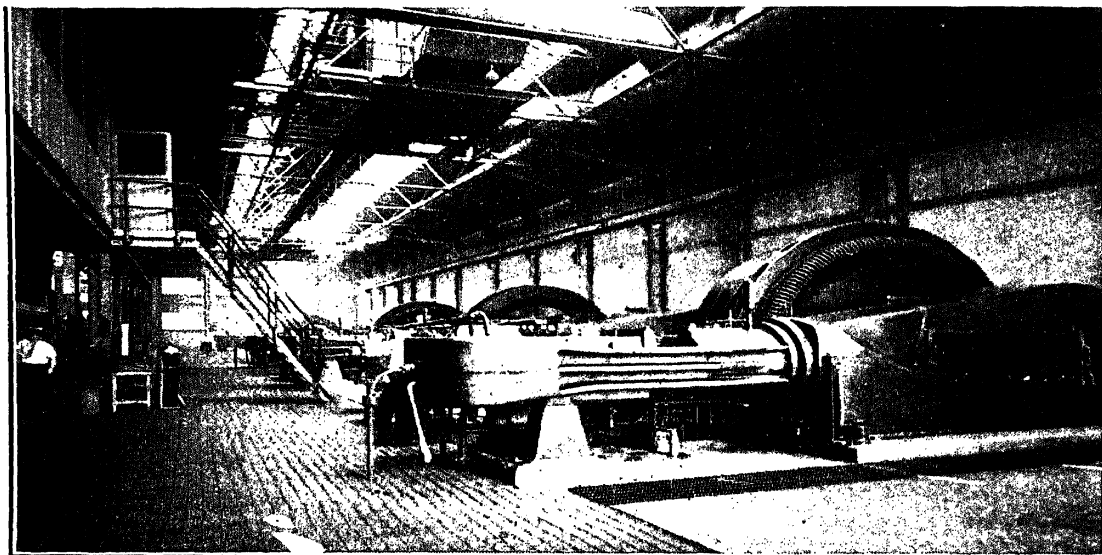
FIGURE 38.—Hypercompressors for direct ammonia synthesis, Belle works, Charleston, W. Va. Each delivers compressed nitrogen plus hydrogen gas at the pressure of 7½ tons per square inch. (Courtesy of E. I. du Pont de Nemours & Co., Inc., Ammonia Department, Wilmington, Del.).

A small amount of ammonia is formed, condensed to the liquid state in the cold water condenser immediately following it. This condensed ammonia retains all impurities which the contact substance itself does not fix, so that the gas issuing from the condenser and separator is of the required purity. This gas is now fed to the high-efficiency converter, where the main conversion takes place; its contact material is maintained at a temperature of 475° C. (887° F.).

The Catalyst. The heart of the process is the converter, and the essential part of the latter is the contact substance. For the American system, exact knowledge of its nature is available.[5] The high-efficiency

[5] U. S. Patent 1,489,497 to Alfred T. Larson.

catalyzer consists of iron oxide granules containing the "combined promoters", potassium and aluminum oxides; the proportions are approximately 1 per cent potassium oxide and 3 per cent aluminum oxide, based on the weight of iron oxide. The preparation of the catalyst is as follows:[6] Iron oxide, which may be prepared by burning pure iron in oxygen, is fused in an electric furnace; to prevent contamination, the hearth of the furnace is made of natural magnetite; the combined promoters are added to the fused mass, in the proportion given above. After the furnace has cooled, the oxide catalyst is removed, crushed, and sieved to give granules of uniform size. These are placed in the converter; the first portions of hydrogen gas in the regular mixture of nitrogen and hydrogen reduce the iron oxide to the metal; during this reduction, the granules probably become porous, which means the development of considerable surface. The explanation of the beneficent effect of the promoters is that they prevent sintering, hence preserve the porosity.

The life of the catalyst is about 100 days, after which it must be replaced; raising the temperature to 500° C. (932° F.) shortens the life of the catalyst mass very much.

The Converter. The converter for a 3-ton plant is an upright cylinder of chrome-vanadium steel 21 inches in diameter widening to 24 inches near the top which carries the removable head; the height of the cylinder is 7 feet. It is made of a single forging except for the head which is held in place by nickel-steel bolts. The walls are 3 inches thick. For greater capacities, the dimensions are correspondingly larger (*see* under Claude process). The compressed gas enters the converter at the base and leaves at the top. The converter contains not only the contact substance but also the heat interchanger. In the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$, heat is evolved; as much as possible of that heat is transferred to the incoming cold gases, so that the temperature at which the reaction is to take place may be attained without expenditure of fuel. This is not quite realized, and some supplementary heat must be supplied by means of a coil of resistance wire electrically heated and placed at the base of the interchanger, heating the gas as it enters the contact mass.

The interchanger is placed in the center of the converter, running through the whole height; around it is the contact mass, distributed in three concentric chambers of unequal sizes. A first narrow chamber surrounds the interchanger; a second somewhat wider chamber surrounds the first; the third similar chamber is the widest. The new gases first pass through the interchangers, to be heated. On leaving the central interchanger, the gas passes up the first chamber, down the second, and up the third, then down one coil of the interchanger and up the other to the outlet in the head of the converter. These various passages and the construction are shown in Figure 39. Each coil of the heat interchanger is double; through the central coil the cold gas flows; through the outer

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[a] U. S. Patent 1,554,008; or *Ind. Eng. Chem.*, **17**, 971 (1925).

one the hot gas; no communication between the two gases is possible. The several contact chambers are formed by steel tubes.

The third chamber leaves a narrow passage between itself and the outer wall of the converter shell. It is through this space that the cold gas which has entered at the bottom, streams on its way to the channels leading to the inner coil of the interchanger; this incoming cold gas keeps the shell relatively cool and therefore better able to resist stresses.
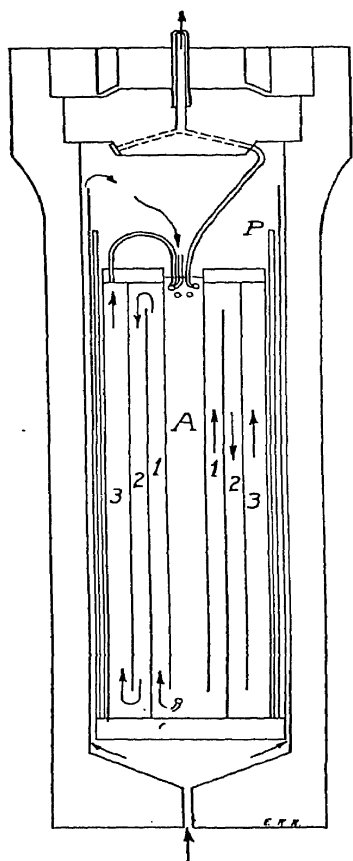

FIGURE 39.—Converter for the American system for ammonia. *A*, space for the two double-walled coils of the heat exchanger; 1, first contact chamber in which the gas travels upward; 2, second chamber, with downward travel; 3, third chamber with upward travel. *P*, Pyrex Glass reflector.

From the converter the gas enters the first condenser, water-cooled, where a part of the ammonia is liquefied. It then enters the circulating pump, lubricated by the liquefied ammonia in the gas. In the main condenser which follows, the cooling is by expanding ammonia, and here all the ammonia in the gas is liquefied. It is collected in receivers and pumped out of these by a liquor line. The receivers act at the same time as separators, the uncondensed gas passing out through a line which brings it to the converter entry. Mixed with fresh gas from the compressor it undergoes partial conversion anew.

There is contraction from 4 volumes to 2 volumes for the portion of the gas which has reacted; in the American process this portion is 30 per cent.

If there is a loss of 10 per cent of the gas volume through leaks and through the loss of unconverted gases when purging the system of argon, there are required 100,000 cubic feet of the gas mixture ($3H_2$ and N_2) measured at 20° C. (68° F.) and atmospheric pressure for each ton of ammonia manufactured. In a plant producing 10 tons per day, which would still be a plant of moderate size, ten times that volume would have to be handled.

The product is obtained in the form of anhydrous ammonia of high purity; it is therefore ready for use in refrigerating plants using ammonia as working medium. In former days a special process was required to change the aqua ammonia made from the gas works liquor into the anhydrous liquid ammonia in steel cylinders. At one time, it was difficult to sell the ammonia from gas liquor for 30 cents a pound, anhydrous, and make a profit; now anhydrous ammonia is quoted at 5 cents (in tank cars). The market for such anhydrous ammonia is limited, and it is therefore invading the fertilizer market in the form of sulfate of ammonia. A tremendous market is opened now that the ammonia is oxidized to nitric acid from which calcium nitrate and sodium nitrate are made, decreasing still further the importance of the Chilean deposits. In the near future, it is likely that all the nitric acid of commerce will be made in this way, and no longer from Chile salpetre. The oxidation of ammonia to nitric acid is described at the end of this chapter.

The Haber Process. The catalyst in this system is promoted iron; the pressure is 200 atmospheres, and the temperature 550° C. (1022° F.). The conversion is comparatively low, about 8 per cent. The process is a complete success, nevertheless. The same company which developed the contact process for sulfuric acid, the Badische Anilin und Soda Fabrik, is also the company which fathered the Haber process; it is now (1937) part of the Interesse Gemeinschaft Farbenindustrie (I. G.), a huge combination of German chemical plants, with an installed capacity of over one million metric tons of nitrogen per year.

While the catalytic conversion is credited to Dr. Haber, the important problem of providing the raw gases cheaply and in the huge volumes required was solved by Dr. C. Bosch. Water gas,[7] made by blowing steam over glowing coal or coke, and consisting essentially of equal volumes of hydrogen and carbon monoxide, is mixed with producer gas [7]; the latter consists essentially of nitrogen, two parts, and carbon monoxide, one part. The mixed gases are mixed still further with steam, and this new mixture is sent through a hot catalyst which causes the water to react with the carbon monoxide to form hydrogen and carbon dioxide; the nitrogen remains unaffected (*see* Fig. 40). The catalyst used in this case is iron oxide containing small amounts of chromium and cerium. The proper volumes are chosen to give at this stage hydro-
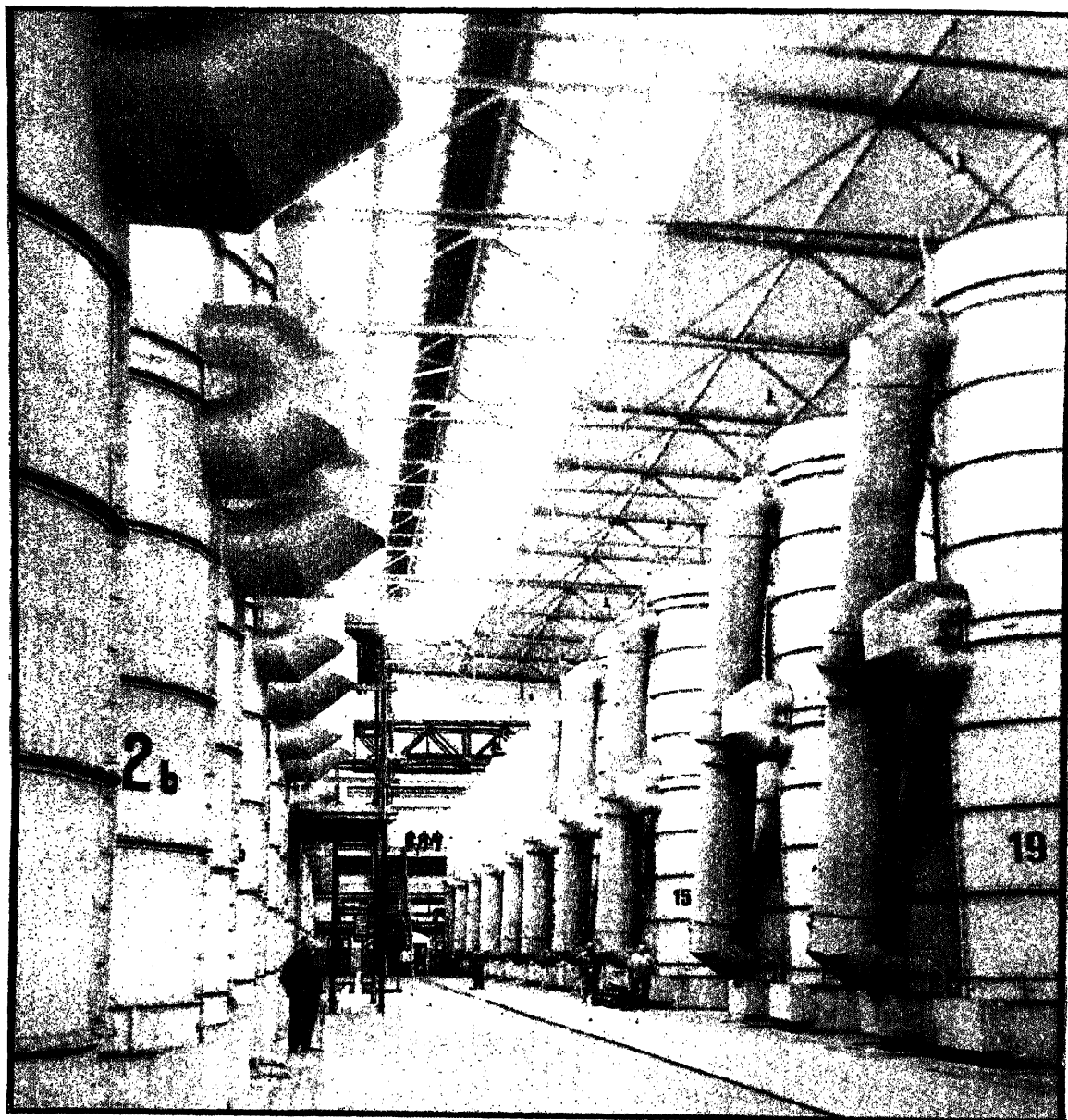
[7] Chapter 15.

FIGURE 40.—Catalytic conversion of carbon monoxide to the dioxide by inter-action with steam in the production of hydrogen for the ammonia syn-thesis, at the Leuna works of the I. G. Each unit consists of a pre-heater, the lower section, and the reaction chamber above it. (Bourke-White Photo, from Pictures, Inc., Chrysler Building, New York.)

gen and nitrogen in the ratio by volume of three to one; but there is present the undesirable carbon dioxide and some carbon monoxide which has escaped the action of the steam. In order to remove carbon dioxide, the gases are put under pressure (50 atmospheres) and scrubbed with water, which at such pressures dissolves carbon dioxide readily; some remains, and is scrubbed out with a solution of caustic soda. The carbon monoxide is removed by scrubbing in ammoniacal copper formate while under the 200 atmospheres pressure which is the working pressure for the catalytic conversion. The cost of the gas mixture by this method is low, so that in the absence of hydrogen as a by-product it will probably be generally adopted.

TABLE 11.—*Sources for Hydrogen for the Production of Ammonia (World).**

Source	1926–27	1933–34
Water gas	89.0%	57.0%
Coke oven gas	3.0	25.0
Electrolysis, water	6.4	16.0
Other**	1.6	2.0

* **Report 114**, *U. S. Tariff Commission*, (1937), p. 41.
** "Other" means electrolysis of brine, fermentation, natural gas.

The converter [8] is similar in principle to the one described under the American system. The proportion of the ammonia in the gas issuing from the converter is so low that mere cooling does not liquefy it sufficiently, and it must be removed by solution in water. The unconverted gases are freed from moisture and circulated through the converter with fresh gas, for further conversion. The ammonia water which is the primary product may be made to give up its ammonia gas very simply by means of continuously operating stills, or in stripping towers, described in chapter one, part one.

The Mont Cenis Process.[9] Similar to the Haber, and of more recent development, is the Mont Cenis direct ammonia process. Use is made of a highly active catalyst (an iron-cyanide complex), which is effective at the comparatively low pressure of 100 atmospheres, and at the temperature of 400° C. (752° F.). The ammonia formed is obtained in liquid form at once.

The Claude System. The Claude system is distinguished by the high pressure used, higher than either the American (in the original form) or the Haber, namely, 900 atmospheres. The source of its hydrogen is coke oven gas. There is present in coke oven gas not far from 50 per cent hydrogen; removing it causes an increase in the Btu. value of the residual gas.

The hydrogen is separated from the other constituents by refrigeration. At the temperature of liquid air (− 180° C. or − 292° F.), only hydrogen remains a gas; it contains some methane and carbon monoxide which escaped liquefaction. The nitrogen is obtained from liquid

[8] **U. S. Patent 1,202,995.**
[9] *Proc. Intern. Conf. Bituminous Coal, 2nd Conf.*, Pittsburgh, Pa., **2**, 202 (1928).

air;[10] it is mixed with the impure hydrogen, the two are compressed to 900 atmospheres in an eight-stage compressor, and passed through a purifier, containing a catalyst which changes the carbon monoxide, at the expense of some hydrogen, to methane and water. The water is removed, but not the methane, for it is harmless to the ammonia catalyst. The hydrogen-nitrogen mixture with its methane content enters a series of converters, four in number; in each some ammonia is formed, and is removed by cooling before the gas enters the next converter. Issuing from the last converter, the unconverted gas contains 10 per cent of methane; all this gas is returned to the original hydrogen separator which produced the first slightly impure hydrogen. From this separator the methane mixed with carbon monoxide is removed in the liquid state, and after gasification is burned under boilers. The portion of the gas mixture (H_2 and N_2) converted in the four converters is 80 to 85 per cent. There is no recirculation of the gas as in the American system.

In order to withstand the high pressure accompanied by the high temperature, which varies between 500° and 650° C. (932° and 1202° F.), a special alloy is used: for example, 60 per cent nickel, 25 per cent chromium, 0.6 per cent carbon, the rest iron; or nickel 60.4 per cent, chromium 8.7 per cent, tungsten 2.5 per cent, carbon 0.4 per cent, and iron 25 per cent. The high temperature means that the catalyst loses its activity rapidly; the active mass must be replaced every 10 or 12 days. The change is made in 5 hours, thanks to the simple construction of the converter.

As advantages possessed by the Claude process might be listed: the handling of more material in a given reaction space compared with processes using lower pressures; a high space-time-yield, made possible by the high temperature which favors rapidity of reaction (see Table 12); the fact that as the activity in the first converter drops somewhat, the second converter functions to a correspondingly higher degree, so that the over-all activity does not fall off.

With converters 27.5 inches in diameter, 11.5 feet high, 30 tons are made per day (900 pounds pressure); with converter tubes 39.37 inches outside diameters, and 13.5 feet high, 50 to 100 tons may be produced. These sizes may be compared to Haber converters, 20 feet high, 4 feet outside diameter with 7-inch walls.

The Casale System. The original development under this system required a pressure of 750 atmospheres, and this has been raised still further of late. One converter is used,[11] and the gas is recirculated frequently. An important advantage of working at such high pressures is that water cooling is sufficient to remove the ammonia formed; another, perhaps more important, is the high conversion obtained, 40 per cent in

[10] Chapter 19.
[11] U. S. Patents 1,408,987 and 1,447,123, both with drawings showing construction of the converter.

a single passage through the converter. Except for the high pressure, this system resembles most the American system.

In 1934, there were 24 Casale plants in operation, of which 10 were in France. Of the 24, 9 were run on hydrogen from coke-oven gas, 10 on electrolytic hydrogen, 3 on water gas hydrogen.

The Fauser Process.[12] This process makes use of the oxidation of a portion of its ammonia in order to furnish its nitrogen for the direct ammonia synthesis. Ten per cent of the ammonia manufactured is mixed with air and passed to a platinum gauze converter. The oxides of nitrogen are scrubbed out and the residual gas saved. It consists mainly of nitrogen, but with a small amount of oxygen. It is mixed with hydrogen and passed over platinized asbestos, so that all the oxygen is changed to water. This latter is removed by cooling, and the purified gas is now pure nitrogen and hydrogen.

Table 12 below permits a comparison at a glance of the various systems for the direct synthesis of ammonia from the elements:

TABLE 12.—*Comparison of Synthetic Ammonia Processes.*

	Pressure atm.	Reported temperature ° C	Reported conversion maximum Per cent	Recirculation of unchanged gases	Catalyst
American	300	475	30	yes	Iron granules, "promoted"
Haber	200	550	8	yes	Iron granules, "promoted"
Claude	900	600	40	no	Iron granules, "promoted"
Casale	750	475	40	yes	Iron granules, "promoted"
Mont Cenis	100	400	40	yes	Iron-cyanide complex

The world installed capacity for direct synthetic ammonia production is distributed among the several processes as follows (1934): Haber-Bosch 35.2, Casale 14.9, Fauser 11.0, Claude 9.4, Imperial Chemical Industries 8.5, Mt. Cenis 8.0, N. E. Corp. 6.5, Gen. Chem. Co. 6.2, American .2.[12a]

The preliminary work included a study of the content of ammonia in a mixture of hydrogen and nitrogen in contact with a catalyzer, at equilibrium. But it must be remembered that in practice the figure for ammonia formation attainable at equilibrium is not reached, because the gases are not allowed enough time to contact with the catalyzer; the conversion must take place rapidly, for the gases stream by at a rapid rate.

In order to make comparisons between runs at different pressures and rapidity of flow, the concept of space velocity is used. Space velocity is the number of liters of exit gas, corrected to 0° C. (32° F.) and atmospheric pressure, which pass over 1 liter of catalyst space per hour. The space velocity for the direct ammonia processes is 40,000 on an average, with variations at the several plants.

Space-time-yield is another useful value; it is the yield of ammonia per liter of catalyst per second.

It should be remembered also that as the pressure is increased, the

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[12] A flow-sheet for the Fauser ammonia system will be found in *Chem. Met. Eng.*, **38**, 628 (1931).
[12a] (From **Report 114**, *U. S. Tariff Commission.*)

volume of the reacting gases becomes smaller, so that a comparatively small catalyst bomb will handle a considerable volume of free gas. (*See* problems at the end of the chapter.)

A number of further statements regarding catalysis will be found in Chapter 25.

FIGURE 41.—Nitrogen industry process-product relationships. [reproduced from report 114, U. S. Tariff Commission, 1937].

Shipments. Liquid anhydrous ammonia is transported in steel tan of various sizes, the standard capacity being 50,000 pounds in a single unit. It is also shipped in steel cylinders containing 25, 50, 100, and 150 pounds of ammonia.

Uses. The main use for ammonia is for fertilizer manufacture in the form of ammonium sulfate mainly, or as ammonium nitrate, phosphate, or as urea. It serves as raw material for manufacturing nitric acid, which transformed into sodium or calcium nitrate also become largely fertilizers.

Ammonia serves the many uses to which an alkali may be put. Anhydrous ammonia is the most important refrigerating agent, because of its low cost and high thermodynamic efficiency. Ammonia is coming into use as a water purification agent, and as nitriding agent for steel. It is an important material in synthetic organic manufactures, such as synthetic urea.

A rather novel use for ammonia is as a source of hydrogen, by passing anhydrous ammonia gas at atmospheric pressure over a catalyst heated to about 600° C. (1112° F.), such as an incandescent Nichrome wire coil. The great advantage lies in the fact that a 100-pound ammonia cylinder, easily transported, yields 3400 cubic feet of hydrogen (mixed with 25 per cent nitrogen).[13]

The Cyanamide Process. In the cyanamide process, ground calcium carbide [14] is placed in iron drums holding each a charge of 4000 pounds, and fitted with a pipe connection so that nitrogen may be fed in. The center of the charge is heated by means of an electrically heated carbon rod and the nitrogen turned on; it is absorbed by the hot carbide, and the reaction evolves so much heat that the carbon rod may be removed after a few minutes; the heat of reaction is sufficient to keep the mass at the reaction temperature. The reaction $CaC_2 + N_2 = CaCN_2 + C$ takes place and continues until after 40 to 60 hours all the carbide is transformed into crude calcium cyanamide. A solid mass results which after cooling is crushed, powdered, and sprayed with water to destroy any unchanged carbide, then with oil to diminish its dustiness. The black powder resulting from the operation contains 60 per cent $CaCN_2$ and is used as ingredient in mixed fertilizers without further treatment.

In a round-about way, nitric acid may be produced from cyanamide, by first making ammonia. The cyanamide is placed in autoclaves 21 feet high and 6 feet in diameter and treated with steam[15]; the generated ammonia may later be oxidized by the hot platinum grid contact method, and the nitric oxide absorbed in water. The ammonia itself may be used in various ways, for instance, to make anhydrous ammonia for refrigeration, sulfate or phosphate of ammonia for fertilizers, and nitrate of ammonia for explosives. The reaction in the autoclave is $CaCN_2 + 3H_2O = 2NH_3 + CaCO_3$.

[13] "Ammonia as a source of hydrogen and nitrogen," J. F. T. Berliner and G. W. Burke, *Trans. Am. Inst. Chem. Eng.*, 25, 42 (1930).

[14] Chapter 17.

[15] A complete diagram of a plant for generating NH_3 from calcium cyanamide will be found facing p. 394, in "The atmospheric nitrogen industry," Bruno Waeser, trans. by E. Fyleman, Philadelphia, P. Blakiston's Sons & Co., 1926.

The nitrogen fed into the carbide charge is made by liquefying air and boiling off the nitrogen in fractionating columns.[16]

Until the advent of the direct synthetic ammonia process, the cyanamide process held a place of importance in the field of fixation of atmospheric nitrogen; at the present time, it seems more likely that it will retain its importance as a process fixing atmospheric nitrogen in the form of the fertilizer ingredient calcium cyanamide, but not as a producer of ammonia and ammonium salts.

By fusion with salt, carbon, and a little carbide, calcium cyanamide may be transformed to sodium cyanide, which in solution is valuable for the extraction of gold and silver from their ores. (*See also* Chapter 18.)

Calcium cyanamide is also the starting material for a number of organic substances such as guanidine, urea, dicyandiamide, which have become of great importance.

The installed capacity for calcium cyanamide in Niagara Falls, Ontario, Canada, was (1934) 80,000 tons of nitrogen per year, which is 14.5 per cent of the world total cyanamide capacity; Germany has 36.7 per cent, Japan, 12.9 per cent of it.

The Bucher Process. Soda ash mixed with iron and carbon may be heated in a current of nitrogen, to produce sodium cyanide and a ferrocyanide.[17] The process at the present time is used in only one plant, in California.

The Serpek Process. Certain metals at elevated temperature unite readily with nitrogen while heated, to form nitrides which in a subsequent treatment with steam give up all their nitrogen in the form of ammonia. The best known of these processes is the Serpek, developed on a fair scale in France. It consists of passing a mixture of crude alumina (bauxite) and coal through a rotary furnace one way, while nitrogen (producer gas) passes the other way. The furnace is heated externally by electrical means to a temperature of 1800° C. (3272° F.). The operation is continuous:

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO.$$
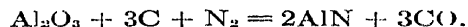
On treatment with dilute alkali, ammonia is formed and at the same time a very pure alumina $AlN + 3H_2O = Al(OH)_3 + NH_3$. If the demand for the by-product were greater, this process would undoubtedly find more general application.[18]

NITRIC ACID FROM AMMONIA

A considerable portion of the ammonia produced by the direct synthetic process is changed to nitric acid by catalytic oxidation. This is now done in the United States in plants with capacity of 300 tons

[16] Chapter 19.

[17] "The fixation of nitrogen," John E. Bucher, *Trans. Am. Inst. Chem. Eng.*, **9**, 335 (1916). For a recent study of this process, see *Ind. Eng. Chem.*, **18**, 43 (1926).

[18] "The fixation of nitrogen as aluminum nitride," H. J. Krase, J. G. Thompson, and J. Y. Yee, *Ind. Eng. Chem.*, **18**, 1287 (1926), contains all the older references.

of acid per day, and it is expected that there soon will be many more. the nitric acid made in this way will fill all the needs formerly supplied by nitric acid from Chile salpetre. The expected exhaustion of the Chilean nitrate deposits is no longer a matter of concern. Since 1925, Germany is absolutely independent of Chile salpetre, supplying her own needs from atmospheric nitrogen processes, with supplies left over for export. The French government plant at Toulouse has a capacity for 80,000 metric tons of sodium nitrate a year, in addition to a large production of ammonium sulfate and other fertilizer materials. The most striking development, however, for the American chemist is this: During 1932, 27 foreign ships loaded cargoes of synthetic sodium nitrate, at Hopewell, Va., taking them to China, Japan, Great Britain, France and Spain.

Oxidation of ammonia by air with subsequent absorption of the nitrous gases in water is performed at ordinary pressure, or under a pressure of 100 pounds. Each has certain advantages. In either case, the principle of the method is that ammonia gas and air mixed (11 per cent NH_3), passed through a fine wire gauze of activated platinum raised to glowing heat, combine to form nitric oxide (NO) and water. The first reaction is $4NH_3 + 5O_2 = 4NO + 6H_2O$. It takes place at a rapid rate, with a 95 per cent conversion, or better; the time of contact is 0.0014 second. The wire is of the fineness of silk. Activation is done by passing a mixture richer in ammonia through the gauze while it is electrically heated. The preliminary activation may be left out, and the gauzes allowed to activate themselves during the first few hours of the run. In the Jones-Parsons converter,[19] the cylinder is 9 inches in diameter and 13 inches on the side; it is suspended so that its long axis is vertical, and its lower opening is closed by a silica piece. The gas mixture enters from above and streams downward through the screen. The wire is 0.003 inch in diameter, while the gauze has 80 meshes to the inch. The preheated gases react and gradually raise the temperature of the gauze to 1025° C. (1876° F.), for the reaction is exothermic. The walls at red heat send back heat by radiation to the gauzes, helping the maintenance of the temperature. The capacity of this converter is $2\frac{1}{2}$ tons of 100 per cent HNO_3 per day, with a conversion of 96 per cent.

The latest design has an aluminum mixing chamber, in order to avoid pre-ignition (*see* Fig. 42). Other designs have a flat horizontal gauze.

The oxidized gases leaving the converter pass through heat exchangers, cooling pipes of chrome steel, and reach the absorption towers fed with water and weak acid, on the counter-current principle. Here, or in some other specially provided space, the oxidation of the nitric oxide to the dioxide takes place, $2NO + O_2 = 2NO_2$. This is a slow reaction; cooling the gases favors it. In the absorption towers, the reaction $3NO_2 + H_2O = 2HNO_3 + NO$ takes place. The NO formed is oxidized

[19] *Ind Eng. Chem.*, **19**, 789 (1927).

to NO_2 again, in the towers, and is gradually all absorbed. The nitric acid from the absorption tower is 50 per cent HNO_3.

Low Pressure System. All the foregoing remarks apply to the low pressure system, which operates at atmospheric pressure. Its main advantage is that the absorption system may be built of stoneware, masonry, or granite, instead of chrome iron, so that the installation cost is less per pound of nitric acid produced; the installation cost for chrome iron pressure system may, however, be no more. In the low pressure system, the general operation is simpler.
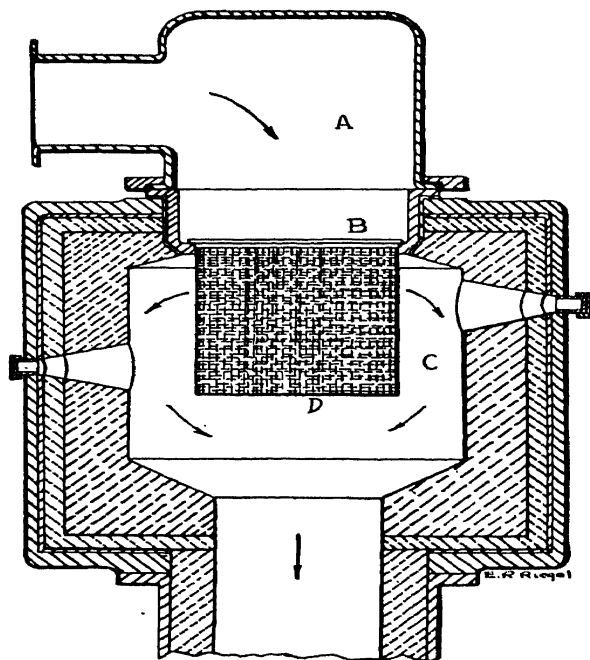
FIGURE 42.—The Chemico ammonia oxidation converter. *A*, mixing chamber, of aluminum; *B*, gauze holder, of nickel; *C*, platinum gauze; *D*, solid silica plate. (Sketched through courtesy of the Chemical Construction Corpn., New York.)

High Pressure System. The high pressure system is operated at various pressures; as an example, 100 pounds may be taken.[20] The absorption system must in this case be of chrome-iron alloy [21] in order to withstand the pressure, but a number of advantages are to be had. The capacity of the apparatus is high. A plant producing 25 tons of acid (as 100 per cent HNO_3) per day consists of one converter delivering finally into a plate tower $5\frac{1}{4}$ feet in diameter and 40 feet high.[22] For the same production, the atmospheric plant requires four burners and 10 towers. The plate tower is cooled at every shelf (with well water), for not only increased pressure but also low temperature favor capacity and strength of acid. In the high pressure plant, 61 per cent HNO_3 is pro-

[20] *Ind. Eng. Chem.*, **23**, 860 (1931).
[21] 17% chromium, less than 0.15% C
[22] A diagrammatic flow-sheet of a pressure plant will be found in reference 20.

duced, while the atmospheric system furnishes 50 per cent acid. The conversion is 93 per cent.

Some of the finer points must be mentioned. During the conversion, there is a loss of platinum, amounting to 5 per cent per month for low pressure operation. When the reaction temperature is raised, which leads to higher conversion efficiency, the loss is increased. With platinum-10 per cent rhodium, the loss is halved.[23] The loss per pound of ammonia burned is not affected by pressure.

To obtain high conversions, the ammonia must be freed by distillation, with filtration of the gas, from the very minute amount of oil it contains; the air must be filtered.[24]

For many purposes, 50 per cent or 60 per cent HNO_3 is satisfactory as to strength; for nitrations of all kinds, it must be stronger. This necessitates an additional operation.

Concentrated Synthetic Nitric Acid. The 50 or 60 per cent HNO_3 is concentrated to 98 or 95 per cent by adding 66° Bé. sulfuric acid, and distilling from a retort; the nitric acid passes out, while the water is retained by the sulfuric acid, which becomes 75 per cent acid. This is concentrated in one of the standard sulfuric acid concentrators. Instead of a retort, a Pauling tower may be used, fed with the mixed acid at the top, and steam at the bottom. Another apparatus is the continuous retort system, "Chemico", consisting of a series of steam-jacketed, acid-proof iron pipes. (*Read also* "Salt Cake" in Chapter 3, and "Nitric Acid" in Chapter 2.)

Synthetic sodium nitrate: The nitric acid from ammonia oxidation may be neutralized with soda ash, to give synthetic sodium nitrate. Caustic residues and comparatively weak lots of acid may be utilized in this way.[24a]

Sodium nitrite is made by absorbing nitrogen oxide in soda ash solution; the method is to mix mother liquor with soda ash solution and treating with the gas. The nitrate-nitrite is crystallized out.[24b] By regulating the air ratio a composition close to the theoretical N_2O_3 may be obtained and comparatively pure nitrite obtained. It is purified by crystallization.

An older method for making sodium nitrite is given in Chapter 31.

Fauser Process [25] for Concentrated Nitric Acid from Ammonia in a Single Step. It is highly desirable to find a way to manufacture the strong acid directly from the gases issuing from the converter, avoiding the concentration by means of sulfuric acid. This is accomplished in the Fauser process. The reacted gases leaving the converter are cooled rapidly, in order to condense and trap away the water of reac-

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[23] U. S. Patent 1,706,055.

[24] Reactions producing elemental nitrogen prevent perfect conversions; such as $4NH_3 + 3O_2 = 2N_2 + 6H_2O$, $4NH_3 + 6NO = 5N_2 + 6H_2O$; $2NH_3 \rightleftharpoons N_2 + 3H_2$, $2NO \rightleftharpoons N_2 + O_2$.

[24a] For sodium nitrate hard pellets, see chapter 8.

[24b] U. S. Patent 2,032,699; the proportion of NO_2 and NO formed from the NO and O_2 and N_2 mixture leaving the platinum converter depends upon the rapidity of cooling.

[25] *Chem. Met. Eng.*, **39,** 430 (1932), with a diagrammatic flow-sheet.

tion. The nitric oxide (NO) first formed remains, for the greater part, unoxidized under these conditions. It passes to an oxidation tower, where NO_2 and N_2O_4 form, then to a cooling tower operated at $-10°$ C. (14° F.) and 10 atmospheres; in addition to the gases, the proper amount of dilute nitric acid is introduced at the top of the tower. There passes out at the bottom a mixture of liquefied N_2O_4 and dilute acid, which is pumped into an autoclave. After the charge is in, the temperature is raised to 70° C. (158° F.), and oxygen, under a pressure of 50 atmospheres, is introduced. In 4 hours, the following reaction, $2N_2O_4 + 2H_2O + O_2 = 4HNO_3 + 18.8$ Cal., has gone to completion; the acid is 98 per cent or better.

OTHER PATENTS

U. S. Patents 1,845,050 and 1,845,068, methods and apparatus for conducting exothermic gas reactions; the incoming gas mixture while being preheated, is in contact with a preliminary amount of catalytic mass. 1,855,040, in which two separate reaction bombs are used, one for purifying and one for producing. Each of these 3 patents has drawings showing construction of converters suitable for the ammonia synthesis. 2,052,326, catalytic converter and ammonia synthesis; 2,010,235, catalytic oxidation of ammonia; 2,018,760, catalyst for ammonia oxidation and the like.

PROBLEMS

1. A direct synthetic ammonia plant produces 1 ton of NH_3 per hour in a catalyst chamber with a catalyst volume of 10 liters. Assuming perfect conversion, and no losses, what is (a) the weight of hydrogen needed; what is its volume at 0° C. and 1 atmosphere? Using the simple gas laws, what is (b) the volume of the same amount of hydrogen as for (a), for the following conditions: 100° C. and 1 atm.; 100° C. and 100 atm.; 100° C. and 1000 atm.; 300° C. and 1000 atm.? The formula to be used is $pv = NRT$, N is the gram mols, R is the gram molecular gas constant and equals 0.082154; T is absolute temperature; p is given, in atmospheres; with these figures, the answer will be in liters. $3H = 3.024$; $NH_3 = 17.032$.
    Answer: (a) 1,791,900 liters; (b) 3761.1 liters at 300° C. and 1000 atm.
    2. The volumes computed in 1 give a good representation of the enormous decrease in volume due to the high pressures, in spite of the high temperature. These volumes are not correct, however, because hydrogen does not follow the gas law exactly. In order to find the true volume, compressibility coefficients must be used, which rest on experiments. By means of the compressibility coefficient, the volume in cc. for one gram of the gas is computed; knowing the weight, the total volume may be obtained readily.**

	Hydrogen	Nitrogen	$N_2 + 3H_2$	Ammonia
0° C. and 1 atm.	1	1	1	1
100° C.; 1 atm.	1.3660	1.3669		1.379
100° C.; 100 atm.	1.4356	1.4121	1.4362	*
100° C.; 1000 atm.	2.0844	2.4948	2.1870	*
300° C.; 1000 atm.	2.8157	3.3203	2.9504	....

* The critical temperature for NH_3 is 132.4° C., the critical pressure 115 atmospheres; explain why the data are missing.

The compressibility factor is used as follows: For 100° C. and 1000 atm., for hydrogen its value is 2.0844. Then

$$v = \frac{2.0844}{1000} \times \frac{22,428}{2.016} = 23.20 \text{ cc. per gram.}$$

Compute the volume for hydrogen for the conditions stated in Problem 1, and list the results opposite the results from 1.

** "Fixed nitrogen," H. A. Curtis, New York, Chemical Catalog Co., Inc., 1932, p. 241.

Answer: For hydrogen, for 300° C. and 1000 atm., corrected: 5045.6 liters.

3. Perform the same computations for nitrogen, and for the mixed gases as represented by $N_2 + 3H_2$. The apparent molecular weight for this mixture is 8.516.

4. With a conversion of 40 per cent, the amount of hydrogen computed above in 1 and 2 is only a part of a larger total. What is this total? What is the volume of the exit gases, expressed for standard conditions (the ammonia assumed to remain gaseous)?

5. In a regular run for direct ammonia, the space velocity is 39,600. The hydrogen-nitrogen gas mixture is 3 hydrogen and 1 nitrogen. The catalyst volume (apparent volume) is 10 liters. The conversion is 40 per cent, and there are no losses. In which period of time will 1 ton of NH_3 be made? And in that period, what is the volume of raw gases which must be sent into the converter, in order to give the performance specified? Express this quantity for standard temperature and pressure (0° C. and 1 atm.); find its volume for 300° C. and 1000 atm., which will be the working conditions, in two ways, first according to the simple gas laws, second, using the compressibility coefficients given under Example 2.

Note: The apparent molecular weight of the $3H_2 + 1N_2$ gas mixture is 8.516.

Answer: 12 hours is the period of time.

6. In the Fauser process for direct ammonia, the reaction for preparing the needed nitrogen is $2NH_3 + 2.5O_2 = 2NO + 3H_2O$. The oxygen brings with itself the nitrogen which air contains. Is the statement and the figure of 10 given in the text correct, and is it per cent by volume or by weight which is meant?

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Until a very few years ago, America mined more phosphate rock than any other continent; that is no longer so. America is outranked in this respect by the dark continent. Man eats lime and phosphates, in order to have the mineral materials for his teeth and bones. The phosphate pebble deposits are the legacy to man from the prehistoric animals, who perhaps did not live in vain, since thanks to their having lived, there is a supply of this essential element (phosphorus) at man's disposal. The same phosphate radicals which perform so useful a function in man's body, performed the same function for the humble dwellers of the earth in the Pliocene, Permian, and other epochs.

Chapter 7

Phosphates, Phosphoric Acid, Baking Powders

The phosphates for fertilizers, for the acid and its products, and for phosphorus come from two sources: bone ash, or mineral deposits, both more or less pure tricalcium phosphate. Bone ash is purer than the mineral material, as one would expect, and serves for making phosphoric acid and monocalcium phosphate for baking powders, as far as its limited supply allows, while the mineral phosphate is the material for superphosphate, of which $3\frac{1}{2}$ million tons were manufactured in 1931, and 3 million tons in 1935 (U. S.).

New deposits of mineral phosphate material have been discovered gradually in the course of the past 50 years; they are indicated by the corresponding production figures listed in Table 13.

TABLE 13.—*Natural Phosphate Production for the World in Metric Tons, (1935).*
(U. S. Bureau of Mines)

Tunisia	1,500,500	
Morocco, French	1,303,182	
Algeria	603,813	
Egypt	473,896	
Africa, total		3,881,391
America, United States		3,091,229
Nauru, Ocean Islands	707,051	
Christmas Islands	147,217	
Curacao	90,709	
Russia	1,167,000	
World total		9,500,000

Within the United States, the mineral phosphate deposits, in the order of their commercial utilization, are: Florida land pebble (30 to 36 per cent P_2O_5), Tennessee brown rock (25 to 37 per cent P_2O_5), Florida hard rock (25 to 37 per cent P_2O_5), Tennessee blue rock (27 to 33 per cent P_2O_5), Western rock (26 to 32 per cent P_2O_5), soft and waste pond phosphates of Florida (15 to 35 per cent P_2O_5), South Carolina phosphate (30 per cent P_2O_5).

As the percentage figures for the phosphoric acid content (P_2O_5) indicate, there is a variation in the quality of the phosphate deposits. High-grade rock contains 70 to 80 per cent tricalcium phosphate; the impurities are mainly clay, limestone, sand and calcium fluoride.[1] The Florida[2] land pebble is high grade, and is found in the bottom of rivers, lakes, and along the banks. The pebbles in the bottom of rivers are gathered by scoops, washed and dried in rotary cylinders, while the banks are mined hydraulically and at the same time the pebbles washed free from clay and earth, then dried. The Tennessee[3] brown rock is also high grade, but has a greater impurity of iron and alumina[4]; both the brown rock and blue rock are actively exploited. The washing is done in a variety of ways, among others by stirring the crushed rock with water and running off the lighter clay suspension. The western rock is somewhat lower in grade, and contains much organic matter (7 per cent); by roasting the rock before using it for superphosphate, the phosphoric acid content is raised, and a waste of sulfuric acid is avoided. All phosphate rock deposits occur in beds a few feet thick; thus for Tennessee, the average is 6 to 8 feet. The Tunisian mine near Gafsa and the Algerian[5] deposit near Tebessa have beds varying from 2 to 10 feet in thickness. Less extensive deposits occur in Spain, and in the Somme region, in France.

The production by states is shown in Table 14.

TABLE 14.—*Production of Phosphate Rock in the United States (1935).*

	Long Tons	
Florida		
Hard rock	121,597	
Land pebble	2,493,463	
Soft rock	39,535	2,654,595
Idaho, Montana		67,490
Tennessee		
Brown, blue, and white rock.....		493,501
U. S. total, 1935		3,215,586
U. S. total, 1934		2,898,238

Superphosphate. Superphosphate is made by the action of chamber acid 50° to 55° Bé., corresponding to 62 to 70 per cent H_2SO_4, on tricalcium phosphate, the essential constituent of phosphate rock. The amount of acid is so regulated that the monocalcium phosphate is formed, soluble in water:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = CaH_4(PO_4)_2 + 2(CaSO_4 \cdot 2H_2O) \qquad (1)$$

<div align="center">

mono-   *gypsum*

calcium

phosphate

</div>
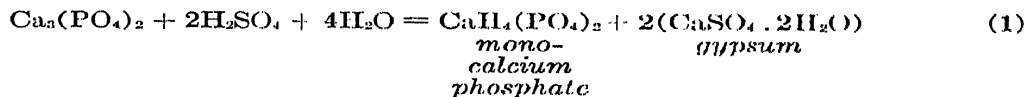
[1] Ratio of fluorine to phosphoric acid is constant, for a given deposit; see *Chem. Met. Eng.*, **21**, 153 (1929).

[2] One district lies along the Charlotte Harbor and Northern Railway which runs through Charlotte, De Soto, Hardee, and Polk counties; another is near Dunellon, in Marion County.

[3] Maury, Hickman, and Lewis counties.

[4] These impurities may be reduced by applying flotation methods; K. D. Jacob, *Ind. Eng. Chem.*, **23**, 15 (1931); in superphosphate, iron and aluminum oxides favor reversion.

[5] *Chem. Abstracts*, **19**, 1551 (1925).

The calcium sulfate in the form of gypsum remains mixed with the monocalcium salt, and it is this mixture which constitutes superphosphate. A certain amount of dicalcium phosphate $CaHPO_4$, insoluble in water, is formed also, and is determined in the analysis by virtue of its solubility in ammonium citrate, in which any unchanged tricalcium phosphate $Ca_3(PO_4)_2$ is insoluble, while the monocalcium phosphate has been removed by water. The mono- and dicalcium phosphates together constitute the "available phosphate" in superphosphate and amount to 16 to 18 per cent P_2O_5.
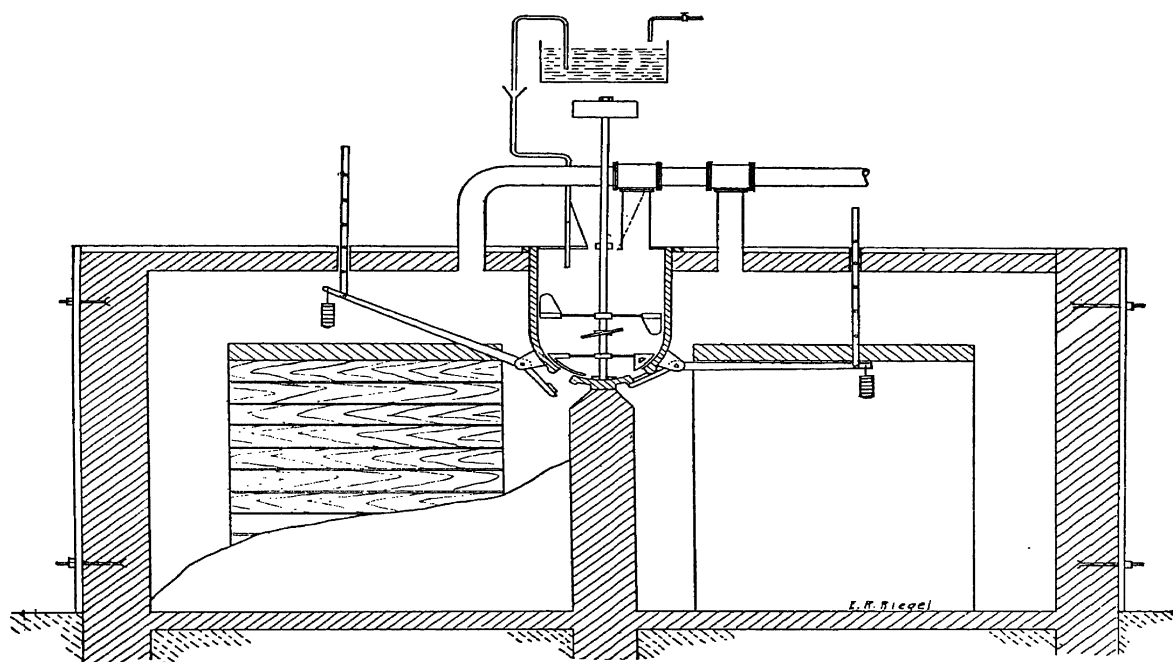
FIGURE 43.—A simple installation for making superphosphate; the mixer serves two pits; outlets for the gases evolved are shown.

What is not generally known is that ordinary superphosphate, and indeed other forms of water-soluble inorganic phosphates, are rapidly converted in the soil into forms which are practically insoluble or are only slightly soluble in pure water. The reaction or reversion results in the formation of water-insoluble calcium, iron and aluminum phosphates, and other insoluble phosphates. These compounds are, nevertheless, able to supply sufficient phosphorus to the soil solution for the growth of plants, due in part to their fine state of subdivision. In general, it may be said that inorganic phosphate fertilizers show very little penetration into the soil beyond the zone in which they are applied, except insofar as this zone is disturbed by plowing and other mechanical means.

In order to make the superphosphate, the rock is reduced to a powder by means of a jaw-crusher [6] followed by a continuous pebble mill,[6] for example. Equal weights of cold acid (first) and powder are run into a cast-iron mixer equipped with paddles, and able to handle 2 tons of rock in each charge. The mass is stirred for 2 minutes, and quickly dumped into the "den" below, where it remains 24 hours; the reaction started in the mixer continues in the den, and causes a rise in temperature to $100°$ C. ($212°$ F.). (*See* Fig. 43.) Carbon dioxide and hydrogen fluoride are evolved, and in passing out, give the mass porosity. The carbon dioxide comes from a limestone impurity $CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$. The hydrogen fluoride originates in the calcium fluoride present in the rock, $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$.[7]

The gases pass out of the mixer and chamber pits under gentle suction, and reach a spray of water in one or more towers. The hydrogen fluoride solution may be neutralized with soda ash, forming sodium fluoride, or it may be treated with more silica (washed sand) to form fluosilicic acid H_2SiF_6; this may in turn be made into sodium or magnesium silicofluoride, the former an insecticide, the latter a preservative for Portland cement surfaces.

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O; \qquad 2HF + Na_2CO_3 = 2NaF + H_2O + CO_2;$$
$$H_2SiF_6 + MgO = MgSiF_6 + H_2O.$$
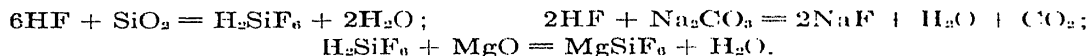
After the 24-hour period in the den, the mass is removed by conveyors and bucket elevators to the storage piles, where the superphosphate is allowed to "cure" for 8 to 10 weeks. By curing is meant the further reaction of free acid on unchanged portions of the rock. The longer the period of "cure," the less the amount of acid one needs to apply. In other plants, there is no curing; the mass from the den passes the "rasper," which divides it into uniform, fine grains, and from there to the storage pile, ready for shipment.

The amount of sulfuric acid added is a little less than required for the main reaction (1), in order to avoid residual unchanged phosphoric acid. The water is ample to allow complete wetting of the powdered rock; a part of the excess remains as water of crystallization, $CaH_4(PO_4)_2.H_2O$, $CaSO_4.2H_2O$; some passes out during the period spent in the den. The superphosphate weighs considerably more than the phosphate rock taken (for example, it may be as much as 1.70 times the weight of the 75 per cent tricalcium phosphate rock taken), because the sulfuric acid added remains in the product in the form of gypsum, while most of the water added also remains. There is a loss in fluorine compounds which pass out, but the extra amount of acid which must be added weighs more than the compounds driven out, so that here again there is a gain in weight. By adjusting the amount of acid, its water content, perhaps its temperature,

[6] Chapter 44.

[7] Some of the hydrogen fluoride attacks the silica impurity, forming the gas silicon tetrafluoride SiF_4 which passes to the towers where it is decomposed by water: $4HF + SiO_2 = SiF_4 + 2H_2O$ and later with the cold water, $3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6$.

to suit the rock used, a product which is dry, which powders easily, and which does not stick in the drill which applies it to the soil, is produced.

It has been proposed to produce a dense, granular superphosphate, whose granules would be mechanically strong, and at the same time shorten the manufacturing process from many days to half an hour. This would be done in a horizontal, rotary autoclave.[8]

Triple Superphosphate. A material with three times as much available phosphate is the triple superphosphate,[8a] containing 48 to 49 per cent P_2O_5. It is therefore a far more concentrated product, offering reduced transportation costs. It is made by the action of phosphoric acid on phosphate rock, instead of sulfuric $Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2$. No gypsum is formed, but instead, more of the soluble calcium phosphate. The acid applied contains 45 per cent P_2O_5, because such strong acid introduces less water which must be evaporated later. The reaction of the rock with phosphoric acid is slower than with sulfuric.

The rock and phosphoric acid are mixed for 1 hour, the resulting solid mass disintegrated and conveyed to the wet storage building; its moisture content is 20 per cent. After an aging period of 30 days, it is dried at a temperature below 200° C. (392° F.), ground in a ring-roll grinder to pass a screen with 6 meshes to the inch. It is a stable, non-hygroscopic powder, with 41 to 42 per cent P_2O_5 in the form of water-soluble phosphate, 48 to 49 per cent P_2O_5 as total available phosphate, combined CaO 20.80 per cent, and moisture 2.75 per cent.

Treating ordinary superphosphate with anhydrous ammonia gas permits the fixation of some 3 per cent NH_3 without increasing the consumption of sulfuric or other acid, gives a product easier to store and apply, which, furthermore, does not rot the containing bags.[9] This has now been extended to treating with urea-ammonia liquor, sodium nitrate-ammonia liquor, and ammonium nitrate-ammonia liquor, with nitrogen content equivalent to 37.5 to 45 per cent nitrogen (compare next chapter).

Soluble Organo-phosphates. Recent work at the University of Nevada Agricultural Experiment Station has been based on the viewpoint that "positional availability" is fully as important as "chemical availability." The ordinary superphosphate already mentioned apparently does not penetrate the soil beyond the depth of plowing or stirring, seven inches to ten inches, whereas the root systems of field and orchard crops feed not only in this surface layer but also extensively below that depth. The effort is now being made to develop organo-phosphates, particularly glucose phosphate, which will retain its solubility long enough to permit it to penetrate into the deeper soil layer, and thus supply phosphorus to the deeper portion of the root system. The successful solution of this task promises not only more efficient application of phosphate to the soil,

[8] U. S. Patent reissue 19,825, of original patent 1,947,138.
[8a] E. L. Larison, *Ind. Eng. Chem.*, 21, 1172 (1929).
[9] K. D. Jacob, *Ind. Eng. Chem.*, 23, 14 (1931).

but also would provide a large outlet for farm products of a starchy nature from which glucose can be made.[10]

PHOSPHORIC ACID

Wet Method. The major part of the phosphoric acid produced for all purposes is still made by the action of dilute sulfuric acid, 30° Bé., on the ground phosphate rock or bone ash $Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O = 2H_3PO_4 + 3(CaSO_4.2H_2O)$. The calcium sulfate is obtained as gypsum. The reaction may be performed in a lead-lined tank with lead-covered agitator, settled, and the clear acid solution containing about 20 per cent P_2O_5 as phosphoric acid, decanted. The mud is washed with water, and the dilute acids obtained concentrated by heat, or used for the dilution of the incoming sulfuric acid from the 50" or 55" Bé. to 30° Bé., ready for treating a new batch. The gypsum may also be filtered in a press, or on sand filters. Improved apparatus is being installed which hastens the separation of the acid from the mud. The Dorr system provides for continuous operation and delivers a first strength of 29 per cent P_2O_5 as phosphoric acid (equivalent to 40 per cent H_3PO_4); a second strength of 15.5 per cent P_2O_5 as acid is employed for the dilution of the chamber or other sulfuric acid. A series of three agitators and six thickeners are used, lined with acid-proof bricks and operated on the counter-current principle; for use in making high-grade fertilizer material, no filtration is required. The mud discharged is free from acid. This artificial gypsum has been utilized for making a number of gypsum products.

When the acid is to be used for baking chemicals, it must be purified from any remaining gypsum, silica, lead, arsenic, iron and aluminum oxides, and fluorine [10a] compounds. The crude acid is colored green; the purified acid is colorless.

Concentration is performed in lead vessels, by means of lead steam coils, to a 45 per cent P_2O_5 strength, or 50 per cent, at atmospheric pressure. Care is taken to avoid overheating, in order to prevent the formation of pyrophosphoric acid, $H_4P_2O_7$. Higher strengths than 50 per cent are more readily obtained by the volatilization process.

The yield by the wet method is about 90 per cent over all.

Thermal Methods. Phosphorus and phosphoric acid may be produced without the aid of sulfuric acid, namely, by thermal methods. On heating tricalcium phosphate in the presence of carbon and silica, elemental phosphorus is liberated which, on oxidation and solution in water, gives phosphoric acid. As heating devices there may be used either the electric furnace or the fuel-fired blast furnace. In either case,

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[10] "Phosphate Studies: I. Soil penetration of some organic and inorganic phosphates," V. E. Spencer and Robert Stewart, *Soil Science*, **38**, No. 1, 65 (1934); *Proc. Second Dearborn Conference*, (May 1936), p. 37, publ. Chem. Foundation, 654 Madison Avenue, New York.

[10a] U. S. Patent 1,858,203 proposes the boiling of the acid with hydrated silica such as diatomaceous earth, followed by the addition of soda ash and decantation from the sodium fluosilicate produced.

the reaction which takes place is $Ca_3(PO_4)_2 + 5C + 6SiO_2 = P_2 + 5CO + 3(CaO.2SiO_2)$. The first product is phosphorus; if it is collected under water, and the oxidation performed later as a distinct step, it is the two-pass system; but if air is allowed to join the phosphorus vapor so that it is at once oxidized to P_2O_5, in the presence of moisture, it is the one-pass system. It should be noted that in the latter, carbon monoxide must also be oxidized, so that the second part of the chemical action is $P_2 + 5CO + 5O_2 = P_2O_5 + 5CO_2$. The solution in water $P_2O_5 + 3H_2O = 2H_3PO_4$ produces the final phosphoric acid.

A flow sheet of the volatilization method, with the source of heat electric, illustrates the one-pass process. (*See* Fig. 44.) The rock or pebble, crushed to small size, is mixed with sand and coke, and fed to an electric furnace with 3 electrodes. The furnace consists of a cylindrical steel shell lined with fire-bricks; the cover has an outlet for the
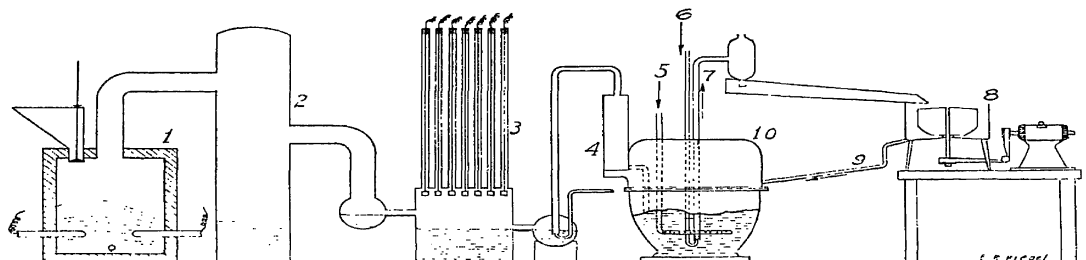
FIGURE 44.—The volatilization process for phosphoric acid, and saturator for ammonium phosphate manufacture; 1, furnace; 2, dust catcher; 3, electrical precipitator; 4, entry of phosphoric acid liquid into saturator; 5, ammonia gas inlet with distributor; 6, compressed air line for continuous ejection of suspension of crystals through 7 to centrifugal 8, with run-back 9 for the clear liquor.

gases which pass through a wet dust catcher to a Cottrell precipitator wherein the phosphoric acid mist is precipitated. The calcium silicate slag passes out of the furnace at the tap hole; given the proper impurities or additions, the slag may be a valuable cement. The flow sheet includes a scheme for making ammonium phosphate.

In the developments [10b] of the Tennessee Valley Authority, the T.V.A., there has been included a fertilizer plant, in which superphosphates are produced. An electric furnace, using about 4,800 kwh. per ton of P_2O_5 charged, sends its gases, phosphorus and carbon monoxide, (a), to be oxidized together, wasting the carbon monoxide, and giving phosphorus pentoxide, which is then hydrated to the acid; or (b), to a cooler where the phosphorus is condensed as a liquid under water, allowing the carbon monoxide to be burned usefully by itself. The phosphorus is then oxidized and hydrated later by itself. The absorption of the P_2O_5 in 85 per cent phosphoric acid runs smoothly and is full of promise.

[10b] "The manufacture of phosphoric acid by the electric furnace method," Harry A. Curtis, *Trans. Am. Inst. Chem. Eng.*, **31**, 278 (1935) with illustrations, flow sheet (p. 282), and diagrams.

The temperature at which reduction takes place is 1300° to 1400° C. (2372° to 2552° F.); 40 per cent of the total heat supplied raises the charge to 1300° C. (2372° F.); the 60 per cent which causes the reduction must be supplied above 1300° C. This the electric furnace does well. On the other hand, the extremely high heat of the arc may volatilize lime, silica, alumina, magnesia; a number of ingenious dispositions and inventions have been necessary in order to prevent this difficulty.

In the blast furnace, 2.36 pounds of coke are consumed for each pound of phosphorus pentoxide P_2O_5 produced. The yield for the thermal methods is 80 per cent; phosphorus is lost to iron and other impurities left in the furnace.

Phosphorus pentoxide is a white powder, extremely hygroscopic. Phosphorus is a yellow, wax-like solid, which melts at 44° C. (111.2° F.); it is kept under water, for in the air it oxidizes spontaneously to its white powdery oxide.

The thermal methods have the advantage of permitting the manufacture of any strength phosphoric acid desired; the higher strengths are obtained without the necessity of concentrating by heat. The acid produced is, furthermore, much purer.

Trisodium Phosphate. Trisodium phosphate, $Na_3PO_4.12H_2O$, is an alkaline substance which has come to be highly prized as a detergent, a water-softener, and boiler compound. It is made in two steps. First, phosphoric acid is neutralized with soda, with the formation of disodium phosphate: $H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + CO_2 + H_2O$. The third hydrogen atom in phosphoric acid is unaffected by soda ash. To the solution of the disodium phosphate, caustic soda is added, with the formation of the trisodium salt: $Na_2HPO_4 + NaOH = Na_3PO_4 + H_2O$.

In a 4000-gallon tank with agitator, 7000 pounds of soda ash are suspended in 900 gallons of hot water or hot wash liquor; phosphoric acid of 45 per cent P_2O_5 content in the proper amount is added at the surface, so that the carbon dioxide evolved may escape more readily.[11] The solution is boiled to remove all carbonate, diluted with mother liquor from previous crystallizations, and filter pressed hot. In the next step, 1500 gallons of disodium phosphate solution (14.5 per cent P_2O_5 and 13 per cent Na_2O) are treated with some 2800 pounds of sodium hydroxide dissolved in 300 gallons of hot water, and then 1000 gallons more of the disodium liquor of the same strength. The resulting solution is diluted with mother liquor from the crystallizer to a specific gravity of 1.34 to 1.40 at 90° C. (194° F.). It is filter pressed, and delivered through steam-jacketed pipes to water-cooled crystallizers; the liquor fed in has a temperature of 70° C. (158° F.) and contains 9.25 per cent P_2O_5 and 13.2 per cent Na_2O. The temperature is reduced gradually to 30° C. (86° F.). The crystals formed are centrifuged, dried in a jacketed rotary drier, cooled, and screened.

A spray-congealed grade is made by adjusting the concentration to

[11] "Trisodium phosphate, its manufacture and use," Foster D. Snell. *Ind. Eng. Chem.*, **23,** 470 (1931).

match that of $Na_3PO_4.12H_2O$, and atomizing at the top of a tower; during the free drop of 70 feet, the particles assume a spherical shape and congeal. The product is screened.

To reduce caking, a small amount of another salt (NaF, NaCl) may be added.

The preparation of disodium phosphate has been given incidental to the manufacture of trisodium phosphate, at least as far as its solution. In order to obtain the salt, this solution is crystallized, the crystals centrifuged and packed. Disodium phosphate is $Na_2HPO_4.12H_2O$ and effloresces (loses crystal water) in the air. It is a valuable agent for water softening. The monosodium salt is also made, but in smaller quantities; this is an acid substance, and serves among other ways as a baking chemical. By heating the monosodium phosphate NaH_2PO_4, sodium acid pyrophosphate, with better keeping qualities, is obtained: $2NaH_2PO_4 + heat = Na_2H_2P_2O_7 + H_2O$.

The production for the sodium phosphates in 1935 was:

	Tons	Price per ton
Trisodium phosphate	87,108	$ 44.35
Disodium phosphate	35,434	37.80
Metasodium phosphate	5,147	100.6
Monosodium and pyrophosphate	4,517	184.2

Monocalcium Phosphate. Monocalcium phosphate is manufactured in considerable quantities, chiefly as a baking chemical. It is made from the purified phosphoric acid, by the addition of selected hydrated lime or limestone: $2H_3PO_4 + CaCO_3 = CaH_4(PO_4)_2.H_2O + CO_2$. After mixing, the materials are set aside to allow the reaction to become complete; the resulting product is a solid, which is crushed to a medium size. It is then dried at a gentle heat, which causes the loss of the water of crystallization. The dry product is milled to the desired granulation, and packaged; it is practically pure monocalcium phosphate.

Dicalcium phosphate is obtained as a by-product in the manufacture of ossein; *see* Chapter 36.

Ammonium phosphate has the advantage of supplying two of the necessary elements for plant food in a single substance. Monoammonium phosphate is made by passing ammonia into strong, hot phosphoric acid until the composition corresponding to $NH_4H_2PO_4$ has been reached; on cooling, a rich crop of crystals form which are centrifuged and dried to a stable, white powder, of formula $NH_4H_2PO_4$. The flow sheet for phosphoric acid by volatilization illustrates the preparation of this salt.

The *diammonium phosphate*, containing some of the mono salt, is more difficult to prepare. Both are made in increasing quantities, with synthetic ammonia. In 1935, 28,900 tons of ammonium, phosphate (Amophos) were produced and used in making fertilizers.

Consumption statistics on phosphoric acid and its compounds are given in Table 15.

TABLE 15.—*Annual Consumption of P_2O_5 in Form of Phosphoric Acid, Phosphate Salts, and Triple Superphosphate (But Not Ordinary Superphosphate), All Phosphoric Acid Products.**

	Tons
Phosphoric acid, all grades	6,500
Monocalcium phosphate	21,500
Ammonium phosphates	3,700
Disodium phosphate	14,500
Trisodium phosphate	15,600
Sodium acid pyrophosphate	1,100
Triple superphosphate (for fertilizers)	18,000
Total	80,900

The figure for the triple superphosphate is only for the phosphoric acid consumed as such in making 60,000 tons of triple superphosphate (at 45 per cent P_2O_5).

* William H. Waggaman, *Ind. Eng. Chem.*, **24,** 984 (1932).

BAKING POWDERS

Baked goods owe their light structure to the presence of carbon dioxide evolved within the dough during its preparation and the early stages of baking. The carbon dioxide may be produced by yeast (bread) or by baking powders (cakes); the latter generate the gas more rapidly, partly at once on being mixed and moistened, the rest on application
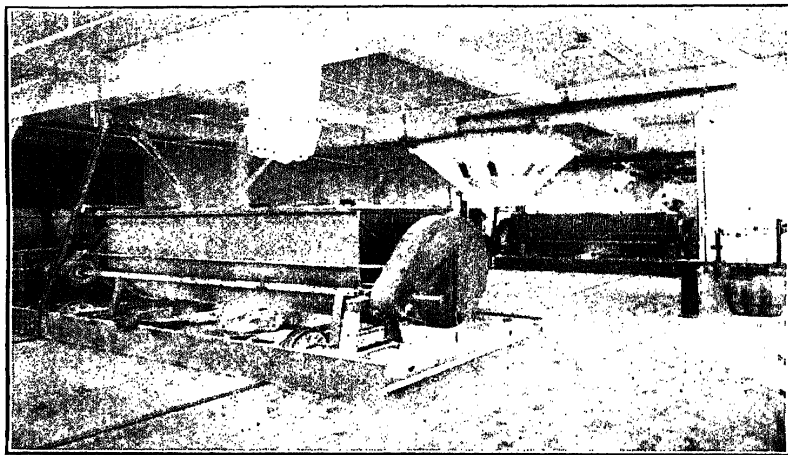
FIGURE 45.—Mixers and weighing hoppers for ingredients for baking powders. The mixers contain 5000 lbs. of baking powder. Note that the mixer is on wheels and may be moved to any one of the bins. (Courtesy of the Rumford Chemical Works, Providence, R. I.)

of heat. A baking powder then is a combination of chemicals, called the baking chemicals, which yield the carbon dioxide gas on being moistened. The amount of gas is calculated to be 14 per cent (by weight) for household powders and 17 per cent for commercial powders. The standardization is performed by selecting the materials too strong, and diluting them to the right strength by the addition of cornstarch. After gas evolution, the residual chemicals must be without harmful action on the human physiological system. Figure 45 shows the equipment for mixing and weighing the ingredients.

Three types of baking powders are estimated to constitute 90 per cent of all the baking powders produced (U. S.); their quantitative formulas to yield 14 per cent CO_2 are as follows:

| | Cream of tartar | Calcium acid phosphate | S.A.S. phosphate |
		——Per cent——	
Sodium bicarbonate	26.73	26.73	26.73
Cornstarch	22.40 (1)	39.84 (2)	40.07 (3)
Tartaric acid	5.97	....	....
Cream of tartar	44.90	....	....
Monocalcium phosphate	....	33.43	13.28
Sodium aluminum sulfate (calcined)	....	....	19.92

In addition to these three, a fourth type (4) is sold to commercial bakers, often in the form of the separate unmixed ingredients; when made up, it contains 30.59 per cent sodium bicarbonate, 29.03 per cent cornstarch, and 40.38 per cent sodium acid pyrophosphate, $Na_2H_2P_2O_7$. This powder evolves 17 per cent gas.

It will be noted that all baking powders have the same carbon-dioxide-generating chemical, $NaHCO_3$, and differ only in the acidic substance. The reactions are probably as follows:

$$KHC_4H_4O_6 + NaHCO_3 = KNaC_4H_4O_6 + CO_2 + H_2O, \text{ for powder (1)}$$

$$3CaH_4(PO_4)_2 + 8NaHCO_3 = Ca_3(PO_4)_2 + 4Na_2HPO_4 + 8CO_2 + 8H_2O,$$
$$\text{for powder (2)}$$

$$Na_2Al_2(SO_4)_4 + 6NaHCO_3 \longrightarrow 6CO_2 + 4Na_2SO_4 + 2Al(OH)_3,$$
$$\text{for part of powder (3)}$$

$$Na_2H_2P_2O_7 + 2NaHCO_3 = Na_4P_2O_7 + 2CO_2 + 2H_2O, \text{ for powder (4)}$$
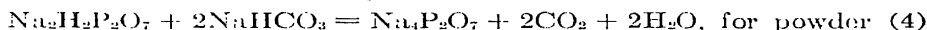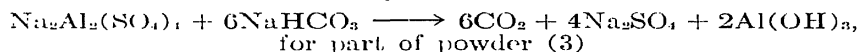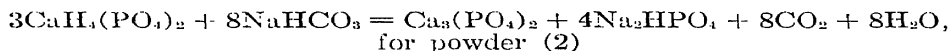
The manufacture of the baking chemicals has been described in the preceding chapters, except for cream of tartar, $KHC_4H_4O_6$, and tartaric acid, $H_2C_4H_4O_6$. Both are solids, and by-products of the fermentation of wine, during which a deposit forms, called argol. It is collected, dissolved, filter-pressed, decolorized by passing through bone char, and the clear liquor crystallized in shallow vats. The product, after drying and powdering, is pure cream of tartar, $KHC_4H_4O_6$.

Wine lees contain, besides the potassium salt, much of the calcium salt; by treating with sulfuric acid, the calcium is precipitated as sulfate, and the mother liquor may be crystallized to give tartaric acid $H_2C_4H_4O_6$, or, written out to show its structure, HOOC.(OH)HC. CH(OH).COOH. This tartaric acid and the tartrates described are exclusively the dextro-rotary isomers.[12]

Cornstarch is presented in Chapter 23.

The production of baking powders of all kinds for the year 1935 was 155,723,766 pounds, valued at 9.3 cents a pound; yeast and other leavening compounds for the same year amounted to 181,005,938 pounds, valued at 7.8 cents a pound.

[12] The unraveling of the various forms of tartaric acid was the first achievement of Louis Pasteur, in 1852.

Other Patents

U. S. Patents: 1,688,112, on trisodium phosphate and its manufacture; 1,633,213, on the use of trisodium phosphate in cleaning, whitening, filling and weighting fabrics; 1,758,448-9, on ammonium phosphate by leaching raw phosphate with an acid; 1,878,997, manufacture of phosphates and phosphoric acid using H_2SO_4; 1,845,876, alumina and alkali phosphates by decomposition with caustic alkali; 1,822,040, diammonium phosphate; 1,831,653, leaching phosphate rock with HNO_3; 1,837,284, producing soluble phosphate using SO_2 and nitrogen oxides; 1,753,478, dicalcium phosphate using by-product HCl on phosphate rock; 2,055,332, purification of sodium metaphosphate; 2,062,866, making sodium phosphate; 2,069,182, the application of sulfonated oil to the mineral concentration for Florida phosphate débris; 1,991,916, method and apparatus for oxidizing phosphorus; 1,988,387, production of phosphorus; 1,869,941, 1,837,329; 1,947,138, reissue 19,825, a rapid method for manufacturing superphosphate.

Problems

1. Seven tons of phosphate rock containing 76 per cent tricalcium phosphate are acidulated with 50° Bé. sulfuric acid (62.18 per cent H_2SO_4), in order to prepare ordinary superphosphate. Taking just the right amount of acid for the reaction with the phosphate, how many pounds will be required? Leaving the reactions with calcium fluoride and calcium carbonate out of account, and assuming that there remains a moisture content of 2.3 per cent, what will be the weight of the produced superphosphate? The new compounds formed are $CaH_4(PO_4)_2 \cdot H_2O$ and $CaSO_4 \cdot 2H_2O$.

2. What is the percentage of P_2O_5 in the rock described in Problem 1? Making the assumption again that the reaction runs as the theory requires, what is the percentage of P_2O_5 present as water-soluble phosphate in the finished product? What would it be, if you started with 100 per cent tricalcium phosphate?

3. A shipment of 87 tons of Florida land pebble phosphate contains 34.96 per cent P_2O_5 in the form of tricalcium phosphate, and 3.92 per cent F in the form of calcium fluoride. The limestone impurity is 7.7 per cent, and the remainder is clay, silica and moisture. What is the composition of the rock, as far as this information indicates it? What is the exact amount of 50° Bé. sulfuric acid which will be required, all reactions proceeding as required by the theory? How much gypsum will be formed in all? Let all the fluorine escape as HF, how much hydrofluoric acid in the form of 60 per cent acid will be collectable, in pounds? What is the weight of carbon dioxide evolved, and how much will the final product weigh, moisture to be again 2.3 per cent?

4. Sulfuric acid of 30° Bé. strength (34.63 per cent H_2SO_4) is to be used for making 9 tons of 40 per cent phosphoric acid (H_3PO_4), equivalent to a 29 per cent P_2O_5 content (1.254 sp. gr.). A low-grade calcined rock with 27.6 per cent P_2O_5 content is used. How much sulfuric acid will be required, and how much rock? How many gallons of 40 per cent phosphoric acid will be obtained? The yield must be taken as 88 per cent.

5. A shaft furnace produces 47 tons of 85 per cent phosphoric acid (H_3PO_4) per day. The coke required is 2.36 pounds per pound of P_2O_5 produced. How much coke is required per day? The yield is 80 per cent over all; how much 75 per cent tricalcium phosphate rock will be needed? If all the phosphorus pentoxide produced in the yield was first collected as yellow phosphorus, how many pounds were there?

6. The 7000 pounds of soda ash under trisodium phosphate (see text) are made into disodium phosphate, without additions. How many pounds are obtained (in solution), and how many pounds of 45 per cent P_2O_5 phosphoric acid were required? How many pounds of 98.6 per cent NaOH must be added to form the trisodium phosphate, assuming perfect recovery? If the product crystallizes with $12H_2O$, how many pounds are obtained, and what is the percentage of sodium phosphate in the crystals?

7. One-half ounce of baking powder of Formula (2) will generate what weight of CO_2, and what volume will the gas have at room temperature?

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"Superphosphate, its history and manufacture," Walter C. T. Packard, *Chemical Age*, 36, 917 (1937).

"Superphosphate process made continuous," *Chem. Met. Eng.*, 44, 30 (1937), a short article, illustrated.

The knowledge of the requirements of vegetation rests on chemical science; on this knowledge in turn rests the choice of fertilizing agents. A considerable part of the fertilizers used are produced, or at least modified, by industrial chemical operations. With the aid of commercial fertilizers, the productivity of a given area may be raised, and a greater number of people may be supported by its yield.

Chapter 8

Fertilizers, Mixed Fertilizers, Potassium Salts, Natural Organic Fertilizers, Synthetic Urea

The greater part of the food supply of the human race comes from the soil, in the form of vegetables and grains, or of meat from domestic animals fed on the products of the cultivated soil. Plants need the following substances for their growth: water, nitrogen compounds, phosphorus compounds, and potassium compounds, in fair quantities; lime, iron, magnesium and sulfur compounds in small quantities. The observation that soils become exhausted by successive crops was made many centuries ago; in order to prevent this exhaustion the ancients allowed a field to "lie fallow" every third season. During that period the particles of rock in the soil weathered and became soluble, furnishing an extra amount of plant food which was ready for use in the succeeding season. Potassium from the feldspars and, to a lesser extent, phosphates from the phosphate rocks, were thus accumulated in the soil; the same process goes on to-day. The ancients also knew the use of manure and the fact that to plant certain grasses and plow them into the soil enriched it. Manure is still used to-day, and crops of clover are grown and plowed under in order to enrich the soil with nitrogen compounds. Wood ashes were used, and supplied, as is now known, potassium carbonate. Thus the merit of modern fertilizing science is not that it has discovered the process, but rather that it has explained it. The particular elements furnished by manure, wood ashes, or clover, are known, and supplies of the necessary foods are furnished by mines and factories in almost limitless quantities.

In stable manure, the nitrogen compounds are chiefly urea, $NH_2.CO.NH_2$, and ammonium salts; manure supplies at the same time organic materials which form the "humus" which every fertile soil contains. Manure is a by-product of the farm and need not be purchased, hence its general use. It is supplemented by nitrogenous compounds from various sources, such as: ammonium sulfate from ammonia recovered during the distillation of coal, or made from synthetic ammonia; synthetic urea; sodium nitrate from Chile, or synthetic; calcium and other nitrates made by nitric acid resulting from the oxidation of synthetic ammonia; calcium cyanamide. The manufacture or method of extraction of these substances will be found discussed under the appropriate head-

A.D. 1842.—N° 9353.

Lawes' Improvements in Manures.

NOW KNOW YE, that in compliance with the said proviso, I, the said John Bennet Lawes, do hereby declare that the nature of my said Invention, and the manner in which the same is to be performed, are fully set forth and ascertained in and by the following Specification thereof (that is to say):—

Whereas bones, bone ash, bone dust, and other phosphoritic substances 5 have been heretofore employed as manure, but always, to the best of my knowledge, in a chemically undecomposed state, whereby their action on the soils to which they have been applied has been tardy and imperfect. And whereas it is in particular well known that in the case of a large proportion of the soils of this country the application of bone dust is of no utility in pro- 10 ducing crops of turnips, on account of the slow decomposition of the bone dust in the soil, and the consequent exposure of the young plant for a long period to the ravages of the turnip fly.

Now, the first of my said improvements consists in decomposing in manner following the said bones, bone ash, bone dust, and other phosphoritic substances 15 previous to using them for the purposes of manure. I mix with the bones, bone ash, or bone dust, or with apatite or phosphorite or any other substance containing phosphoric acid, a quantity of sulphuric acid just sufficient to set free as much phosphoric acid as will hold in solution the undecomposed phosphate of lime, whereby the free phosphoric acid is enabled to unite itself at 20 once with the various alkaline earths contained in the soil, and the undecomposed phosphate of lime is left in a state of division far greater than can be effected by any mechanical means.

The second of my improvements has relation to manures applicable to soils deficient in any particular alkali, as potass, or soda, or magnesia, or ammonia. 25 For such soils I make use of a manure compounded of a mixture of phosphoric acid with the particular alkali required, as potass, or soda, or magnesia, or ammonia, or any earth containing such alkali.

The third and last of my said improvements relates to soils from which a crop of wheat or any other plant of which silica forms an essential component 30 part is intended to be raised. For such soils I make use of a manure composed of a combination of silica, either in the state of ground flint or sand, with either of the alkalies, potass or soda, or composed of crystal or glass ground to a state of powder.

And having now described the nature of my said invention, and the manner 35 in which the same is to be performed, I declare that I have not stated any particular proportions in which the different materials are to be employed as aforesaid, and do not confine myself to any particular proportions, because such proportions must vary in each case with the relative strength of the substances

FIGURE 45a.—A page from the British patent 9353, issued to John Bennet Lawes in 1842, the first practical application of Liebig's discovery that phosphates mixed into the soil would promote the growth of plants. In a disclaimer filed later, Lawes restricted his claims to the treatment of the "phosphoritic substances with brown sulphuric acid of commerce."

ings. Other important sources of nitrogen in suitable compound form are dried blood (13 per cent N), tankage (from garbage), sewage disposal sludge, bone meal, dried albumen, dried fish scraps, oil meal such as pressed cottonseed meal which for one reason or another cannot be used as cattle food, and a number of other materials of animal origin.

Phosphorus is applied in various forms. Finely powdered phosphate rock is applied directly,[1] to the extent, for example, of 50,000 tons in 1929; it is insoluble in water, but weathers fast. Superphosphate with 16 to 18 per cent P_2O_5 is used to a far greater extent; its phosphate is soluble, and therefore of immediate service to the plant. Triple superphosphate, with 48 per cent P_2O_5, is gradually coming into use.

The slag from the Thomas and Gilchrist process[2] contains calcium phosphate which is insoluble in water, but which weathers more readily than the tricalcium phosphate in phosphate rock; it is applied directly to the soil, after powdering. The content of iron is high (7 to 10 per cent iron oxides), but does not interfere with the fertilizing properties. The slag is very hard and must be powdered in a special ball mill with hard steel balls. Slag phosphate is of no importance in the United States, but it is used in Europe.

Precipitated tricalcium phosphate is absorbed by the plant more rapidly than the rock phosphate; a very finely divided tricalcium salt is the "colloidal phosphate" from Florida.[1] Another important material supplying phosphorus is bone meal.

Potassium salts, chiefly the chloride, are obtained from deposits in the earth, from brine ponds in arid regions, and other sources, as fully discussed in this chapter; they are sold in various grades or strengths, reported on the basis of potassium oxide K_2O, a convenient way to rate them.

Mixed fertilizers contain nitrogen as nitrates, urea, ammonium salts or other nitrogen-containing compounds; phosphorus as superphosphate, and potassium salts, chloride or sulfate; the order given above is the one generally used, so that a 2-8-2 fertilizer would contain 2 per cent nitrogen, 8 per cent phosphoric acid anhydride (P_2O_5), and 2 per cent potassium oxide, K_2O. The formulae differ for the several crops: for late potatoes, 4-8-10; wheat, 2-12-6; sugar beets, 4-12-6; clover, 0-12-15; strawberries, 5-8-7. This method of evaluation in terms of nitrogen, phosphoric acid, and potassium oxide is merely for convenience; the compounds actually present are those given above. Sodium nitrate (Chilean) may be mixed with superphosphate, or applied singly. The mixed fertilizer usually contains some inert material, such as earth or gypsum; its function is mainly to dilute, but also to act as a drier, preventing the caking of the powder.

The mixing of "complete" fertilizers is done in a revolving mixer not unlike a cement mixer, or in any other type mixer found suitable; the

[1] K. D. Jacob, *Ind. Eng. Chem.*, **23**, 15 (1931).
[2] Chapter 48.

several ingredients are dumped (horse-drawn cart) into a hopper; a bucket elevator feeds the mixer. The batches are of several tons each.

The complete fertilizers refer to nitrogen, phosphoric acid (as P_2O_5) and potassium oxide; but while these three elements are the most important, it might be mentioned that there must be present 10 elements in the ground for successful growth of plants; they are: phosphorus, nitrogen, potassium, calcium, sulfur, magnesium, iron, carbon (in large part from the atmosphere), hydrogen, and oxygen.

The fertilizing values may be concentrated by manufacturing for example ammonium phosphate, which would contain both the nitrogen and the phosphoric acid, or potassium nitrate, containing potassium and nitrogen. For long shipment, high concentrations are desirable, since the freight on inert matter is saved. The wider use of concentrated fertilizers promises to be the next great development in this field.

Ammoniated Superphosphates. There has come into prominence of late the method of spraying a very strong ammonia, as for example a hydrous ammonia with 40 to 80 per cent NH_3, onto a charge of superphosphate contained in a revolving mixer, so that new surfaces are continually exposed. The relation may be 5 parts of NH_3 to each 100 parts of superphosphate (18 per cent P_2O_5). The ammoniated superphosphate has an increased value; also any residual sulfuric acid is neutralized, and the "rotting" of the bags from that cause is avoided. A mixed fertilizer may also be ammoniated by means of very concentrated hydrous ammonia, delivered from a steel pressure tank similar to the anhydrous ammonia containers. For example: superphosphate 900 pounds, sulfate of ammonia 52 pounds, manure salts 267 pounds, filler (sand) 673 pounds, total 1892 pounds, may be treated with 108 pounds of NH_3 in the form of 40 to 80 per cent hydrous ammonia. The anhydrous material is rarely used, for a certain quantity of water seems to be necessary in order to produce the essential grain structure, and avoid the undesirable powder structure which anhydrous ammonia brings about.[2a] This new development is a result of the decreased price of ammonia, from the 25 cent level of a decade ago to below 6 cents a pound of NH_3.

As logical extensions of this practice there is now marketed, and increasingly favored, the use of a urea-containing ammonia liquor (since 1932) containing 15.1 per cent nitrogen in the form of urea, and 30.4 per cent as ammonia (NH_3), with a total of 45.5 per cent nitrogen. Rivaling this is the sodium nitrate-containing ammonia liquor with a total nitrogen content of 44.4 per cent, and ammonium nitrate in ammonia liquor, with a total of 37.5 per cent.[2b] About 180 pounds of the urea-ammonia liquor and 400 pounds of the ammonium nitrate-ammonia liquor can be added to a ton of superphosphate without causing reversion.

The ammoniation of superphosphates in this way has been a distinct advance in the science of fertilizer manufacture.

[2a] U. S. Patent 2,060,310.

[2b] Compare p. 57, report 114, U. S. Tariff Commission, described under reading references; also booklets "Urea-ammonia Liquor-A" (1933) and "UAL-B," (1936) DuPont Company, Ammonia Department, Wilmington, Del.

Sodium Nitrate Solid Pellets. It has been found advisable to alter the condition of Chilean nitrate intended for fertilizer mixing, by forming it into round pellets, in order to remove its hygroscopic property. The method [2c] consists of melting the nitrate at the temperature of not over 350° C. [662° F.], forcing it through a filtering screen, and spraying it into a cooling chamber; there results a product consisting of small balls with a hard outer surface, and solid throughout. Another method [2d] provides for the incorporation of 5 per cent potassium nitrate, magnesium nitrate or ammonium sulfate, giving again a non-hygroscopic solid hard pellet, well suited to the agricultural drill which applies the mixed fertilizer to the soil. This improvement has been carried over into the synthetic nitrate manufacture.

POTASSIUM SALTS

The most extensive mineral deposits of soluble potassium salts are those at Stassfurt, in Germany, which supplied nearly all of the world's requirements until 1914. Since the close of the war, the deposits in upper Alsace (France), near Mulhouse, have been developed until they yield about one-third of the Stassfurt tonnage; they are similar in nature to the German deposits. A third deposit of similar character lies in Poland, near Kalusz in the southeastern part, and yielded 261,310 tons of potassium salts of all grades in 1931. The German production was about $1\frac{1}{2}$ million tons for that year. A fourth producing deposit is the one in Carlsbad, New Mexico, which began shipments in 1931.

The Stassfurt area lies in the central part of Germany, between Magdeburg and Halle. The deposits of the potash beds are at a depth of about 1000 feet, and overlie a bed of salt (NaCl) 3000 feet thick. Over the potash beds a layer of clay separates them from another deposit of salt (NaCl) of more recent geological origin. Three potash layers are distinguished, of which the upper is 300 feet thick and extends over many square miles; it consists of carnallite $MgCl_2 \cdot KCl \cdot 6H_2O$ (40%) mixed with salt (20%) and other impurities. Below the carnallite lies polyhalite $2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$, and below this, kainite $MgSO_4 \cdot KCl \cdot 3H_2O$. The geological history of these deposits is that salt deposited from sea water leaving a mother liquor which gradually gained in potassium salt content; a change in the topography caused the isolation of the bay, and the lake so formed dried completely; it was during this dry period that the potassium salts deposited. A similar relation of solubilities is exhibited by present-day sea water, which is evaporated for salt in the south of France: after the salt has deposited, the more soluble magnesium salts with some potassium remain in the mother liquor, and are run off because the magnesium is bitter.

The method of mining at Stassfurt is by shafts and tunnels. The mineral is dislodged by blasting with black powder; it is loaded in mine cars and hauled to the refining plant at the mouth of the shaft.

[2c] U. S. Patent 1,937,757.
[2d] U. S. Patent 2,021,927.

The German potash salts for fertilizer purposes are produced in four grades. Their value is based largely on the calculated potassium oxide equivalent: kainite, with 12 per cent K_2O; manure salts, with 20 per cent; potassium chloride, with 50 per cent; potassium sulfate, also with 50 per cent.

The crude carnallite is refined to potassium chloride by treating the crushed material with a hot solution of 20 per cent magnesium chloride, from a previous operation. In this solution, the salt (NaCl) is insoluble, and is left behind with calcium sulfate and other impurities; from this solution, potassium chloride deposits on cooling. The mother liquor is concentrated and gives on cooling a lower grade of potassium chloride utilized as manure salts. The first crop of potassium chloride may be refined further by washing with cold water; this further treatment is applied only to a limited quantity.[3]

FIGURE 46.—Map of the Permian potash field in Texas and New Mexico. (Courtesy of the Department of the Interior, U. S. Geological Survey.) The dots and numerals mark test drilling locations.
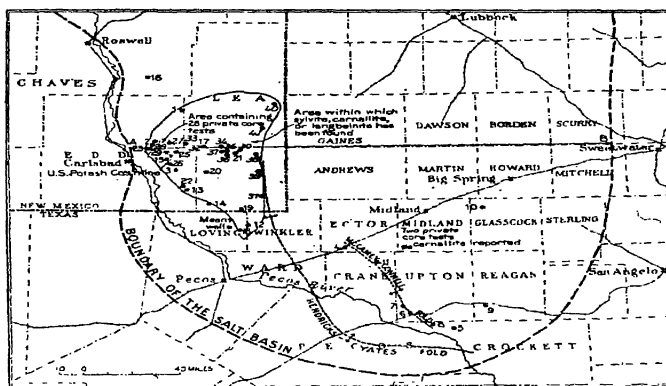
The Alsatian deposits[4] consist of two strata. The upper one is about 3 feet thick, and contains 35 to 40 per cent potassium chloride; the depth is 1500 feet below the surface in one section, but greater in others. The lower layer is 7.5 to 16 feet in thickness, and lies about 50 feet lower; it contains 24 to 32 per cent potassium chloride. Both layers are essentially sylvinite, $KCl \cdot NaCl$, containing sodium chloride as impurity, and clay; the purification is by crystallization, and leads to potassium chloride 98 per cent pure (or with 61 per cent K_2O content). Lower grades are obtained from mother liquors; a part of the mine product is shipped after mere crushing. The grades marketed are: Sylvinite, 12 to 16 per cent K_2O; sylvinite rich, 20 to 22 per cent or 30 to 32 per cent; potassium salt (*sel de potasse*), 40 to 42 per cent; and potassium chloride (*chlorure de potasse*), 62 per cent K_2O. The first two are crushed mineral; the last two have been concentrated by solution and crystallization.

[3] To the north and northwest of the Stassfurt basin potassium salts are also found, in Hannover, Braunschweig and Mecklenburg; these deposits are smaller, and consist chiefly of sylvine or sylvinite, $KCl \cdot NaCl$, more or less pure.

[4] "The Alsatian potash industry," Henri Vigneron, *Chem. Met. Eng.*, **24**, 655 (1921), with 16 illustrations.

The American deposits lie in the southeastern part of New Mexico, in Eddy and Lea counties, and in the neighboring counties in Texas, Loving, Winkler, Ector, Crane, Upton, Reagan and Crockett. (*See* Fig. 46.) The deposits are of Permian age. The area covers underground deposits of rich potassium salts, chiefly chloride; in Eddy County, there are numerous beds (10) at depths between 800 and 1762 feet below the surface, varying in thickness from 1 foot 2 inches to 4 feet 6 inches, and having an arithmetical total of 36 feet. (*See* Fig. 47.) The potassium minerals are sylvinite (the richest), kainite, and some polyhalite. At a depth of 1267 feet, the bed is 3 feet 6 inches of sylvinite; at 1311 feet another deposit of 3 feet occurs, consisting of sylvinite and polyhalite; while at 1365 feet depth, a 2-feet thick bed of sylvinite is available. A shaft sunk near Carlsbad, New Mexico, serves a mine operating since 1931; in that year, a large tonnage was produced, with a content of 25.6 per cent K_2O. The mineral was higher in potash than the test cores had indicated.
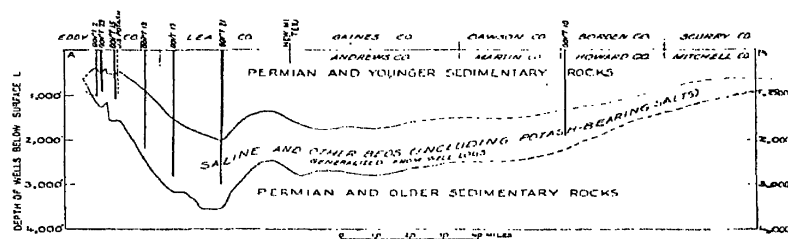
FIGURE 47. Projected section of Permian potash field in Texas and New Mexico. (Department of the Interior, U. S. Geological Survey.)

In addition, there are numerous beds of polyhalite, an impure potassium sulfate, averaging close to 10 per cent K_2O, at depths of 1100 to 2752 feet under the surface.[5] The thickest bed is 15 feet 6 inches, at a depth of 1459 feet, with 8.8 per cent K_2O, in Eddy County. The deepest down is in Winkler County, Texas, where at 2267 feet depth, a bed of 9 feet 8 inches occurs, with 7.23 per cent K_2O, and just over it, at 2257 feet depth, a layer 6 feet thick is found, with 10.63 per cent K_2O. The richer mineral tapped by the Carlsbad shaft has not been found in the Texas counties.

A refinery has been erected at Carlsbad, N. M. (Potash Company of America) in which a flotation method is used for the separation of potassium chloride from its valueless companion in sylvinite, sodium chloride. The production is near 100,000 tons of KCl, with 60 per cent K_2O.

The New Mexico and Texas deposits were probed during and since the war, by private citizens and by government agencies. The Mulhouse deposits are due solely to private enterprise; they were discovered while searching for petroleum, before the war.

Potassium Salts from Brines. Besides the important mineral de-

[5] Regarding the possible exploitation of the polyhalite beds, it might be noted that potassium in the form of the sulfate is the preferred form for the fertilization of the citrus fruit crop. H. H. Storch, *Ind. Eng. Chem.*, 22, 934 (1930); Everett P. Partridge, *Ind. Eng. Chem.*, 24, 896 (1932).

posits of Stassfurt, Alsace, southeastern Poland, New Mexico and Texas, brines from lakes in dry areas furnish potassium salts. Of the numerous enterprises begun within the United States during the war to relieve the shortage due to the blockade of German seaports, only one survived, that of the American Trona Company at Searles Lake,[6] in the dry desert between California and Nevada. This lake is really a deposit of solid salts with a brine permeating them; the salts are stiff enough to carry a dirt road. The brine is pumped to the plant, concentrated in triple-effect evaporators 86 feet high, in which common salt precipitates; the concentrated liquor on cooling deposits crude potassium chloride, which is refined to contain 60 per cent K_2O. Borax is produced from the same brine, by agitating it, after the potassium salts have deposited in the quiet liquor. The output per year is about 50,000 tons of high-grade potassium chloride. Up to a few years ago, the bulk of the world's *borax* was produced from colemanite, $Ca_2B_6O_{11} \cdot 5H_2O$, by decomposing with boiling sodium carbonate, filtering and crystallizing. Development of Searles Lake brine with its additional products of potassium chloride and sodium sulfate made it possible to produce borax cheaper than from colemanite. However, at about the same time, extensive deposits of rasorite, $Na_2B_4O_7 \cdot 4H_2O$, were discovered near Kramer, California, which are now mined, the ore shipped to Los Angeles Harbor, dissolved in water under heat and pressure, strained, filtered and crystallized as pure borax, $Na_2B_4O_7 \cdot 10H_2O$.[6a]

The production of crude borates from all sources was 272,967 tons, valued at $21.40 a ton (U. S. 1935).

A similar brine from a drying salt lake near Zarzis in Tunis is the basis of a growing industry.[7] The exploitation of the brine in the Dead Sea is now under way. The production is to be at the rate of 1000 tons annually for nine years, then 50,000 annually for the next ten years. The relative sizes of the sources already discussed may be indicated by the reserves, figures for which are as follows: Stassfurt, 8 billion tons

[6] *Searles Lake.*

Composition of Searles Lake Brine.

NaCl	16.35	Per cent by weight
Na_2SO_4	6.96	
KCl	4.75	
Na_2CO_3	4.74	
*$Na_2B_4O_7$	1.51	
**Na_3PO_4	0.155	
NaBr	0.109	
Miscellaneous	0.076	
Total Solids	34.65	
Water by diff.	65.35	

* Equiv. to 2.86 per cent $Na_2B_4O_7 \cdot 10H_2O$.
** Equiv. to 0.067 per cent P_2O_5.

The American Potash and Chemical Corporation uses vacuum crystallization extensively, (see Perry, "Chemical Engineers Handbook," p. 1486), saving space, circulating water, and material in process. Heat exchangers are used everywhere, utilizing the heat of vaporization of vapors from the crystallizers, heats of solution of various salts, and other heats. This is one of the outstanding examples in the country of the practical application of solubility diagrams, phase rule, and other physico-chemical data.

See furthermore *Ind. Eng. Chem.*, 10, 839 (1918).

The American Trona Corporation is now the American Potash and Chemical Corporation, 233 Broadway, New York.

[6a] *Chem. Met. Eng.*, 42, 430 (Aug., 1935).

[7] *Chem. Abstracts*, 13, 2737 (1919).

K_2O; Mulhouse basin, 350 millions; Dead Sea, 2 billions, and Searles Lake, 20 millions.

There are other mineral sources of potassium. Alunite $K_2Al_6(OH)_{12}(SO_4)_4$ is mined and worked for potassium sulfate in Sulphur, Nevada, and Marysvale, Utah. On roasting, the aluminum sulfate is decomposed, and the potassium sulfate may be leached out.[8] Leucite $(KNa)AlSi_2O_6$ is successfully worked for potassium in Italy by means of hydrochloric acid. Greensand of New Jersey (Odessa, Del.), shales in Wyoming and other states, and feldspar, contain potassium. The nitrate deposits of Chile contain potassium, and there is now recovered a 25 per cent KNO_3 material, by means of a special process; in case of necessity, this method of working could be applied to all the Chile nitrate produced, and with normal production, approximately 300,000 tons a year potassium nitrate could be obtained. Other deposits are in Spain, Abyssinia, Canada and Russia.

In 1935, 76.4 per cent of the world production of potassium salts from minerals or brines was the German-French one, and of that production, the United States imported 13.9 per cent.

Aside from minerals and brines, potassium salts are obtained by collecting the flue dust which passes out of the cement kiln,[9] by means of a Cottrell precipitator; it is estimated that 2 to 5 lbs. of K_2O may be recovered for each barrel of cement made. For the iron blast furnace similar installation indicate that 17 lbs. of K_2O may be conserved for each ton of pig iron manufactured. The ashes from fermented molasses residues, ashes from the spent pulp of the sugar beet (7000 tons yearly), wool washings, and kelp[9] are commercial sources for potassium compounds.

Potassium nitrate may be used for fertilizing; it has the advantage of combining two of the essential elements. Formerly the extraction of potassium nitrate from the upper layer of the soil near stables was of some importance (India); the constant reformation of nitrate is due to the growth of bacteria. Potassium nitrate may be made by double decomposition of potassium chloride with sodium nitrate: $KCl + NaNO_3 = KNO_3 + NaCl$. Solid potassium chloride is added to a strong hot solution of sodium nitrate; sodium chloride first separates, then on cooling, potassium nitrate crystallizes.

Another method is to pass nitrogen peroxide into a potassium chloride solution.[10]

In the Kooban province in southern Russia, extensive plantations of sunflowers furnish stalks which are ashed and then extracted for potash; the production is over 20,000 tons a year.[11]

Potassium salts are also in demand in the chemical industries, for the reason that the potassium salts crystallize well as a rule, while the sodium salts do not. As a result, it is easier to separate potassium compounds

[8] *Ind. Eng. Chem.*, 10, 838 (1918).
[9] *Ind. Eng. Chem.*, 10, 834 (1918).
[10] *Ind. Eng. Chem.*, 23, 1410 (1931).
[11] *Chem. Met. Eng.*, 30, 501 (1924).

from other reaction products than it is to separate the corresponding sodium compounds. Purification by crystallization is also easier for potassium compounds than it is for sodium compounds. Examples of potassium salts manufactured on the industrial scale in preference to the sodium salts merely because the former crystallize with ease, are: potassium permanganate, dichromate, chlorate, and ferricyanide. In some cases, the potassium compound is preferred because the corresponding sodium compound is hygroscopic; in still others, because of the specific action of potassium, differing from that of sodium.

The United States are still importers of potash salts; in 1935, 603,595 tons of salts were imported, with a content of 241,510 tons of K_2O. The domestic production from all sources was 357,974 tons of salts, equivalent to 192,793 tons of K_2O. It is estimated that the capacity of the present mines and plants is sufficient to supply the domestic needs. Imports will probably continue in the coming years, because the cheap ocean freight rates give German-French potash an advantage on the Atlantic coast, and because the low-grade salts seem cheap to the agriculturist, although on the basis of K_2O content, they may be dearer than the more concentrated form. *See* Table 16 for world production statistics.

TABLE 16.—*World Production of Potash in Metric Tons of K_2O (1935)* (*Bureau of Mines*).

		Per Cent of Total
Germany	1,393,000	61.1
France	347,300	15.3
United States	174,897	7.7
Spain	121,372	5.3
Poland	71,539	3.1
Palestine	12,000	.5
All other	10,000	.4
Total for world	2,280,000	....

NATURAL ORGANIC FERTILIZERS

By-products of the packing industry which are of value as fertilizers are dried blood, bone meal, and tankage. The fish industry contributes fish scrap. In a number of other industries there are by-products which serve primarily as cattle feed, but if, for any reason, they are unacceptable for that purpose, they may be of value as fertilizing agents.

In the slaughter house, the blood is pumped to a coagulating tank with a conical bottom. It is cooked until coagulated, and of the consistency of liver. On standing a few hours, a separation takes place; water settles out at the bottom and is drawn off. The coagulum is pressed, dried, and powdered; it forms a dark reddish meal. It is either sold as such, or it is mixed with potash salts and phosphates to make a rich fertilizer.

Bones are cooked in open tanks, or steamed under pressure; in either case, grease is removed. The degreased bones are crushed and powdered.

Tankage is used primarily for feeds; it is a brown meal, containing 9.5 to 11 per cent nitrogen as NH_3 and 12 to 20 per cent of bone phos-

phate of lime. Applied to the soil, tankage decomposes more slowly than dried blood. Fertilizer tankage is produced from meat scraps, intestines, bones, and carcasses of dead or condemned animals, by cooking under a steam pressure of 40 lbs. for 4 to 12 hours. Grease and tallow float to the surface and are removed; the solids are separated from the tank water, and ground. The tankage still contains 10 to 20 per cent grease which is generally removed by naphtha, before it is sent out as a fertilizer.

Guano is a mixture of birds' excrements and fish bones and other fish refuse, found on certain islands off the Peruvian coast, where the rainfall is slight. The deposits are surface deposits and are still in process of formation, but their importance as to tonnage has decreased. Their quality has also decreased as the materials rich in urea and ammonium oxalates are practically exhausted. Guano is found and mined in other localities.

A nitrogenous material is produced from activated sludge in sewage disposal plants; such a material is Milorganite, described in Chapter 13.

SYNTHETIC UREA

A nitrogenous material of synthetic origin is synthetic urea $NH_2 . CO .$ NH_2; in solution its formula is more probably $HN : C \! < \! \begin{array}{c} NH_3 \\ | \\ O \end{array}$. Its nitrogen content is remarkably high, namely 46.6 per cent for the pure substance. It is being manufactured in Germany and in the United States on a large scale. The suitability of synthetic urea as a plant food is just as good as that of the natural urea in manures.

The process of Carl Bosch and Wilhelm Meiser [12] consists in passing the mixed ammonia and carbon dioxide gases, with some moisture, into an autoclave held at 130° to 140° C. (266° to 284° F.); ammonium carbamate $NH_2.CO.ONH_4$ forms first, and is transformed into urea. (Fig. 48.)

$$2NH_3 + CO_2 \rightleftharpoons NH_2 . CO . ONH_4 ; \text{ and then,}$$
$$\text{ammonium carbamate}$$

$$NH_2 . CO . ONH_4 \rightleftharpoons NH_2 . CO . NH_2 + H_2O.$$
$$\text{urea}$$
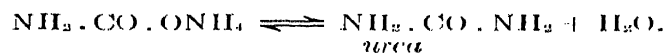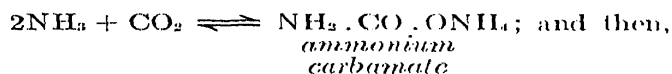
The conversion is about 40 per cent, and there is discharged from the autoclave, continuously if desired, a melt which is introduced directly into a plate still. Steam enters at the base, and drives out the uncombined ammonia and carbon dioxide, while a solution of urea is discharged at the bottom of the still. It is concentrated and crystallized.

The make-up gas may be conveniently introduced by running a solution of ammonium carbamate into the upper part of the column; the gas driven out is compressed in warmed compressors and conveyed by warmed

[12] U. S. Patent 1,429,483.
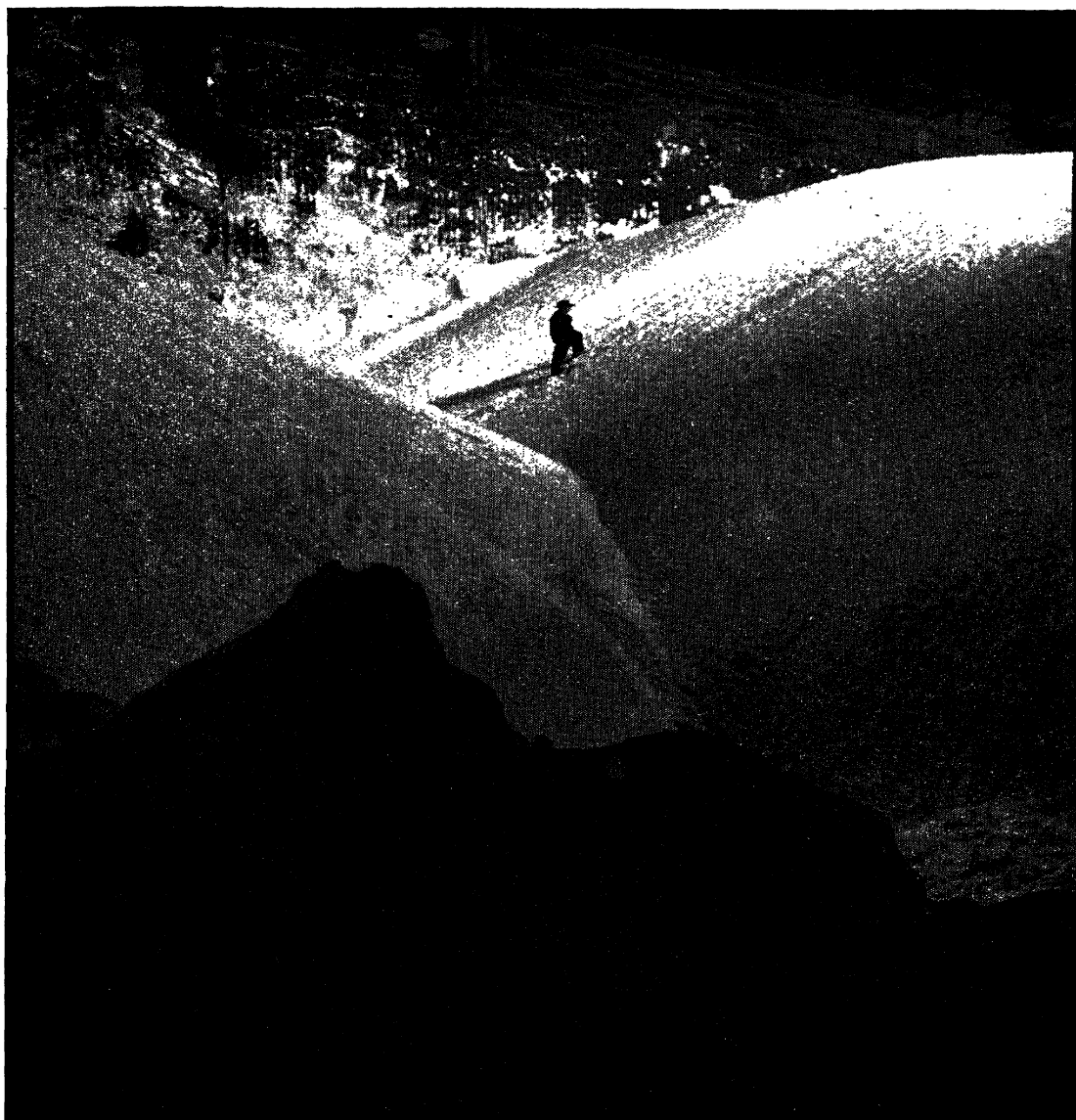
FIGURE 48.—Synthetic urea storage pile, at the Leuna Works, Germany.
(Bourke-White Photo from Pictures, Inc., New York.)

lines to the autoclave, in order to prevent the deposition of ammonium salts.

The Krase process [13] provides for the introduction of liquid ammonia

³ "A direct synthetic urea process," by H. J. Krase, V. L. Gaddy and K. G. Clark, *Ina. Eng. Chem.* **22**, 289 (1930).

and liquid carbon dioxide into an autoclave. Modifications [14] provide for neutralizing unchanged ammonia with phosphoric acid, producing a concentrated fertilizer containing two of the essential elements.

The figures in Table 17 will indicate the relative importance of several fertilizer materials.

TABLE 17.—*Importance of Fertilizer Materials (1935).*
(*Bureau of the Census*)

Fertilizers	Production Tons	Value
Made in all industries	....	$140,386,112
Made in fertilizer industry	....	115,434,862
Made as secondary products	....	6,626,194
Fish scrap	100,211	26.50 a ton
Bone meal	56,313	25.20 a ton
Tankage	203,269	
Superphosphate		
Total	2,998,569	
Produced for sale	1,078,990	9.45 a ton
Other fertilizers	187,832	28.70 a ton

The average price for domestic potassium salts for fertilizer purposes exclusively in 1935 was $12.27 a ton (2000 lbs.), and its average K_2O content 55 per cent.

The average price for all fertilizers, which amounted to 6.2 million tons, was $18.90 a ton in 1935.

The developments in the nitrogen industries are part of a study of the general field of fertilizers; these developments have been presented in Chapter 6, and many statements and figures of primary interest to the fertilizer field are included there.

OTHER PATENTS

U. S. Patent 2,074,880, molecular addition compound of calcium sulfate and urea, $CaSO_4 . 4CO(NH_2)_2$, made by reacting mixtures consisting of calcium sulfate dihydrate and urea in a saturated aqueous urea solution. The following U. S. Patents have been assigned to the Tennessee Valley Authority: 2,037,306, on manufacture of ammoniated superphosphate; 2,040,081, agglomeration of fine phosphate rock; 2,043,328, manufacture of dicalcium phosphate; 2,044,774, treating phosphate rock to eliminate fluorine.

PROBLEMS

1. What is the highest percentage of K_2O which any potassium chloride preparation can contain?

2. One hundred tons of mineral containing 59 per cent of carnallite pass through the refinery and are made into crude potassium chloride containing 48 per cent K_2O. If the recovery is 72 per cent, how many tons of crude potassium chloride will be obtained?

3. Fixed nitrogen in the form of 96 per cent urea totaling 1000 metric tons of nitrogen are ordered. How many pounds of material will have to be shipped? Make the same computation for commercial ammonium sulfate, Chilean nitrate, assuming for each 96 per cent purity.

4. 2000 pounds of rasorite carrying 85 per cent $Na_2B_4O_7 . 4H_2O$, are dissolved, filtered, and run to the crystallizer as a 25 per cent solution of borax, $Na_2B_4O_7 . 10H_2O$, at 150° F. After cooling to 100° F., the crystals are centrifuged and go to the drier carrying 5 per cent moisture.. The mother liquor contains 8 per cent borax. What yield of dry crystals is obtained?

[14] U. S. Patents 1,797,095; 1,782,723.

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The manufacture of Portland cement has become an important industry; in 1935, the production was 24.2 million tons, for the United States. Gypsum in the same year was mined to the extent of 2.5 million tons, while the lime produced was 2.5 million tons. These three industries are now recognized as essentially chemical.

Chapter 9

Portland Cement, Lime, and Gypsum Plaster

The tremendous expansion of the Portland cement[1] industry in the last twenty years is due to extensive road-building programs, to the development of reinforced concrete construction, and to the adaptability and uniformity of the material. Cement roads are permanent, and their upkeep practically nil. Reinforced concrete permits the construction for instance of a horizontal platform bridging the space between two walls, capable of carrying heavy loads without other support than itself. Not only walls and piers, but girders of concrete are now freely used. Bridge piers, tunnels, dams, and canal walls are built of concrete as well as sidewalks, steps, garage and factory floors, and building foundations. One reason for the almost universal use of Portland cement is the comparative ease of working it (pouring); another is its strength, which increases with age; a third is its uniformity, which permits calculations of strength as reliable as those made for structural steel.

Portland cement is a greenish-gray, impalpable[2] powder. Its essential constituents are lime, silica, and alumina, which are combined to form tricalcic silicate, $3CaO . SiO_2$, tricalcic aluminate, $3CaO . Al_2O_3$, and dicalcic silicate,[3] $2CaO . SiO_2$; these are unstable compounds, which on being wetted, rearrange, with different speeds. Tricalcic silicate acts rapidly, forming gelatinous calcium hydrate and gelatinous silica, and to this change is due the initial set which occurs in 3 hours; the hydration continues, the gelatinous material binding the grains of sand which are always added, and the crushed stone filler, to a hard mass. Tricalcic aluminate acts with the same rapidity as tricalcic silicate, but does not produce a strong bond. Dicalcic silicate acts only after months have elapsed.[4] The hardening of Portland cement continues for years, and the concrete made from it increases in strength. As time passes, the gelatinous calcium hydrate crystallizes, adding a further element of strength.

In mixing water with Portland cement and stones, to give the con-

[1] The name was given by Joseph Aspdin, because the cement he made in 1824 yielded stones resembling those quarried near Portland, England; his cement is the prototype of the present Portland cement.

[2] No grains can be felt between the fingers.

[3] There are four forms of dicalcic silicate, all of which occur in Portland cement. The major one, however, is β-$2CaO . SiO_2$.

[4] The complete statement regarding the constituents of Portland cement will be found in "Properties of the calcium silicates and calcium aluminates occurring in normal Portland cement," by Bates and Klein. *Technologic Paper* 78, Bureau of Standards, Washington (1917). Two thorough articles on this study are: E. S. Shepherd and G. A. Rankin, *Ind. Eng. Chem.*, **3**, 211 (1911), and G. A. Rankin, *ibid.*, **7**, 466 (1915).

crete, 4 to 8 gallons of water are used per sack of cement; not more than $2\frac{1}{2}$ gallons will chemically combine with each sack of cement, to become part of the structure. The rest evaporates. Too rapid evaporation is undesirable; it is retarded by keeping the surface covered with straw, and by wetting it (curing). The purpose of curing is to prevent evaporation until after hydration has proceeded well along to completion.

The setting of pure Portland cement is so rapid that, uncontrolled, the cement would be useless; the addition of small percentages of calcium sulfate (as gypsum) gives the desired retardation. The initial set of pure cement occurs in 6 minutes; 3 per cent of gypsum lengthens the period to 3 hours.

In the manufacture of Portland cement the proportions of lime (generally as limestone), alumina, and silica (as clay or shale) are carefully adjusted, and the mixture is sintered; in natural cements a suitable rock is generally used without admixture, so that the composition is variable, and there is no sintering. Considerable amounts of Portland cement are made from the iron blast-furnace slag.

Portland cement sets under fresh water as well as in air, it is therefore also a "hydraulic" cement; for sea water, its iron content should be raised to several parts per hundred.

Raw Materials. Limestone and clay are the necessary raw materials; pure limestone is not usually chosen, except for adjusting the final mixture; rather argillaceous limestones, which are more common and which cannot be used for making quicklime, nor in the blast furnace, are used. The "cement rock" is such a limestone, which contains the necessary constituents in proportions so nearly right that only slight adjustments are necessary. The plant is erected as near to the deposit as possible; the rock is hauled perhaps 1000 to 2000 feet in the most favorable cases.[5] The material is blasted in the quarry,[6] and brought to gyratory crushers,[7] which reduce the rock to egg size. The addition of correcting amounts of limestone, for example, takes place at this stage. The properly mixed materials are generally dried in a short (40-foot) rotary furnace with inside heating, then crushed further in a swing-hammer mill,[7] sieved, and finally pulverized in a Raymond suction mill,[7] or similar pulverizer. The material ready for the furnace is of such fineness that 90 per cent will pass through a 100-mesh sieve. The relative proportions of raw materials must be such that the analysis of the final cement falls between the following limits:

			Limits	Average
			Per cent	
Lime	CaO	....	58–65	61.5
Silica	SiO_2	....	20–25	22.5
Alumina	Al_2O_3	....	4–11	7.5
Magnesia	MgO	....	0–4	2.0
Iron	Fe_2O_3	....	0–4	2.0
Sulfur trioxide	SO_3	....	0–1.75	1.0
Alkali	Na_2O, K_2O	....	0–3	1.5

[5] Examples: Bath, Nazareth, Martin's Creek, near Easton, Pa., and Alpha, just across the river in New Jersey.
[6] Which may be a hill, such as at Martin's Creek.
[7] Chapter 44.

Instead of limestone, marl, a deposit of a geologically more recent origin, may be used; in such a case, it is often conveyed, wet, through pipes to the plant, and ground wet; the clay is then also ground wet. In three plants, oyster shells and clay are the raw materials. After mixing and settling, the materials are shaped into bricks which are dried before they are sent to the furnace, or the slurry may be fed directly into the kiln, to be dried by the outgoing gases; in the latter case the furnace is lengthened. Both wet grinding and dry grinding are the practice in the United States, with the 149 operating plants (1935) about equally divided. Limestone and clay are the more frequent combination, roughly 3 parts of limestone to 1 of clay.

During the furnacing there are lost carbon dioxide and water of constitution, so that there is a shrinkage in the material obtained; it is usually estimated that 1.7 tons of raw materials produce 1 ton of cement.

The slag from the iron blast furnace may be so adjusted that it is well suited for the manufacture of Portland cement; it is mixed with limestone, with perhaps another addition to reach the desired percentages, and furnaced as the rock mixtures are. The shrinkage in this case is somewhat smaller.

TABLE 17a.—*Distribution as to Raw Materials of the 1935 Production of Portland Cement in the United States.*

	Per cent of total
Cement rock and pure limestone	31.0
Limestone and clay or shale	58.8
Marl and clay	1.9
Blast furnace slag and limestone	8.3

* Bureau of Mines, Statistical and Economic Surveys.

The Portland Cement Rotary Furnace. The furnace generally used in the United States is a brick-lined steel cylinder, slightly inclined from the horizontal; it is mounted on idling wheels of small diameter, and carries a gear wheel meshing with a pinion wheel which rotates the cylinder at the rate of one-half to two r.p.m. according to size. The operation is continuous, raw material is fed in at the upper, colder end, and the clinker is discharged at the lower, hot end. The flame is formed by pulverized coal, atomized oil, natural gas, and sometimes producer gas, at a burner placed in the stationary hood into which the lower end of the cylinder fits. The hood acts also as receiving box for the discharged material, called the clinkers. An extension of the stationary box reaches into a smaller cylinder inclined from the horizontal in the opposite direction, and also rotated; as a result, the clinkers, after reaching the smaller cylinder through the chute, move forward toward the discharge opening. A current of air sweeps over the clinkers and enters the burner hood, there to become the air of combustion for the fuel; by preheating the air in this way, the temperature reached in the hotter end of the furnace is raised, while at the same time the clinkers are cooled. At the opposite end of the furnace, a similar sta-

tionary hood is provided in which the raw material feed and an outlet for the fire gases are provided. These gases are usually passed under boilers before reaching the stack.

The size of the furnace has been constantly increased. Originally the external diameter was 5 feet, the length 60 feet; since then, furnaces with a diameter of 10 feet and a length of 240 feet have been built and operated with complete success. The intermediate sizes, 100 to 150 feet long, are the more common.

As the raw materials travel from the colder end toward the flame, they are gradually heated, on the counter-current principle. The temperature in the various parts of the furnace varies; in general three zones may be distinguished, and in each, a definite process takes place. Referring to the illustration (Fig. 49), zone A is the upper third of the
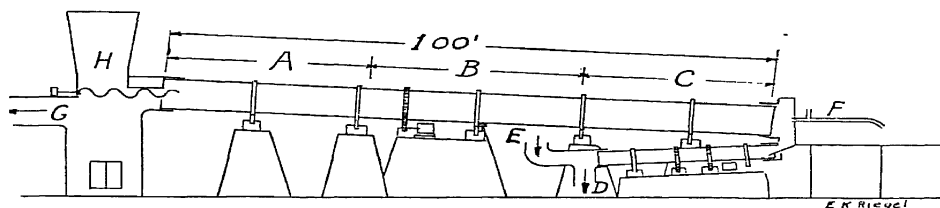
FIGURE 49.—The rotary Portland cement furnace; *F*, pulverized coal burner; *H*, feed bin with conveyor; *D*, discharge of clinkers; *G*, passage for fire gases to boilers and stack; for zones *A*, *B*, and *C*, see text.

furnace, where the materials are warmed to red heat; any remaining water is driven out in this zone. In zone B, the middle zone, the temperature averages 1000° C. (1832° F.); the carbon dioxide is expelled from the limestone. In zone C, the maximum temperature of 140° or 1420° C. (2552° to 2588° F.) is reached; the mass partly fuses in this zone and forms small clinkers, like gravel (incipient fusion); it is in this zone also that the valuable tricalcic silicate is formed. The total time the charge requires in order to pass through the kiln averages one and one-half hours; hence it remains in each zone half an hour, with constant agitation. The flame from pulverized coal or gas is 35 feet long (average) so that essentially all of zone C is at the maximum temperature. The rate of travel of the charge depends upon the rate of rotation of the furnace; faster rotation gives greater output. A furnace 9 feet in diameter and 160 feet long produces about 1000 barrels (at 376 lbs. each) a day.[8] The output of a furnace 10 feet in diameter and 240 feet long, fed with slurry, is probably 1500 barrels a day. The clinkers are discharged into the cooling cylinder below, but even after this cooling they are at red heat and must be left to cool in heaps on the floor. The fuel consumption in the kiln, in the case of coal, is 120 lbs. of the best bituminous coal per barrel of cement produced.[9]

[8] *Ind. Eng. Chem.*, 18, 912 (1926), article by Richard K. Meade.
[9] "Cements, Limes, and Plasters," E. C. Eckel, New York, John Wiley & Sons, Inc., 1928.

After cooling, the clinkers are disintegrated by a swing-hammer mill [10] for instance, and pulverized in a Raymond suction mill [10]; the gypsum is added at the swing-hammer mill. The fineness of the powder is very important; it is made such that 92 per cent passes through a 100-mesh sieve, and 75 per cent through a 200-mesh sieve. The tendency is toward even greater fineness. The cement powder is stored in tall concrete chambers or silos. It is shipped in barrels holding 376 lbs., or bags holding 95 lbs.; the latter retails at 90 cents or less per bag.

Portland cement meets specifications and tests which have become official.[11] The neat (unmixed) cement must have a tensile strength of 500 lbs. per square inch after seven days; the cement mixed with 3 parts of sand must have a strength of 200 lbs. after the same period.
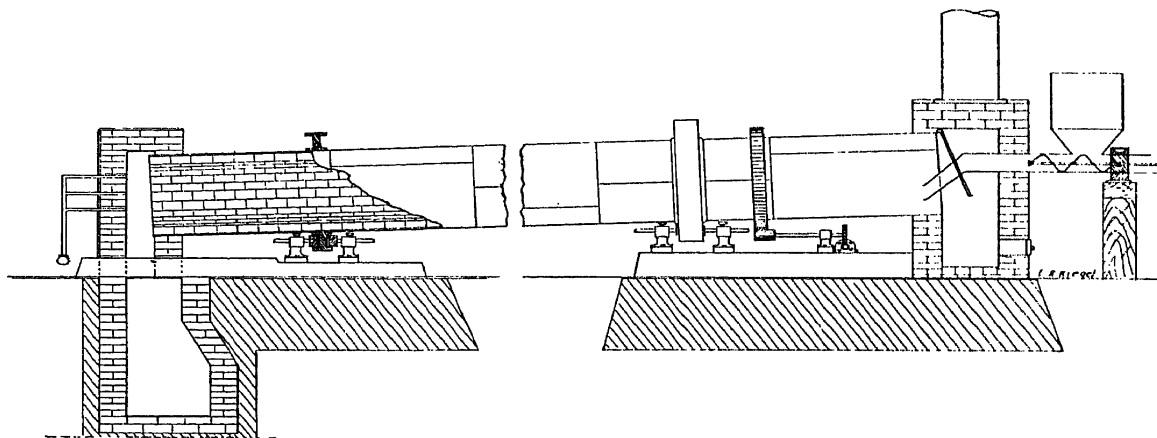
FIGURE 50.—Portland cement furnace with clinker pit, showing furnace lining.

The strength of concrete, which means cement 1000 lbs., sand 1500 lbs., and crushed stone 3000 lbs., is greatly increased by imbedding in it twisted square steel bars, or wire netting similar to fencing; it is then called reinforced concrete.

Magnesium fluosilicate,[12] $MgSiF_6 \cdot H_2O$, in solution, is applied to the surface of cement roads and walls in order to protect them from weathering; such protection is not absolutely necessary, for the cement structure is permanent without it, but the surface becomes smoother and the weather-resistance properties are increased. Pipes for sewers, as large as 5 feet in diameter, are made of concrete, and are harder and stronger if treated with magnesium fluosilicate solution.

[10] Chapter 44.

[11] "Standard specifications and tests for Portland cement; adopted by the American Society for testing materials, and by the U. S. Government," 1917, 47 p., obtainable (10 cents) from the Superintendent of Documents, Washington, D. C. Bur. Foreign and Domestic Commerce, Industrial Standards, No. 1.

[12] Chapter 2.

The recovery of potash from cement furnace gases is discussed briefly in Chapter 8.

A hydraulic cement high in alumina (42 per cent) has recently been introduced; it is stronger than Portland cement and resists the action of sulfate-bearing waters; its durability is not yet established.[13]

There were produced in the United States, in 1935, 76,751,419 barrels of Portland, an increase over 1933, but still less than half the 1929 production, which was 170,646,036 barrels. The average factory price for bulk in 1935 was $1.51 per barrel.

QUICK-SETTING CEMENT OR HIGH EARLY STRENGTH (H.E.S.) CEMENT

If Portland cement be intimately mixed with an additional 15 per cent or more calcium carbonate, and the mixture then burned in the rotary cement kiln, there results a cement which sets to a hard mass, able to bear traffic, in 24 hours, while the standard Portland cement requires 6 to 8 days. Because such cement is sintered a second time, it is often called double-burned cement. An example is Incor, manufactured under U. S. Patents 1,700,032 and 1,700,033. The quality of quick setting is due to a higher percentage of tricalcic silicate. In the standard Portland cement, the several essential constituents have the following percentages:

	Per cent
Tricalcic silicate	50
Dicalcic silicate	25
Tricalcic aluminate	20

In quick-setting cement, the percentage of tricalcic silicate is raised to 70 per cent or so, at the expense of dicalcic silicate, which drops to 5 per cent or so. The rôle played by dicalcic silicate in the setting of the cement is unimportant, as explained in the introduction to the chapter. Two analyses of such cements are given in Table 18, with that of the clinkers and cement from which they are made.

TABLE 18.—*Analyses of Quick-setting Cement and the Cement and Clinker from Which it is Made.**

	Knicker-bocker clinker	Knicker-bocker cement	Durbin cement Quick setting	Houston clinker	Houston cement	Durbin cement Quick-setting
SiO_2	23.46	22.36	20.58	24.60	23.56	21.70
Al_2O_3	5.49	5.64	5.15	5.60	5.94	6.26
Iron oxides	2.89	2.66	3.51	2.72	2.46	2.70
CaO	64.55	63.53	65.31	66.30	63.90	66.20
MgO	3.13	3.14	3.18	.83	.84	.86
SO_3	.12	1.72	1.51	.13	2.03	1.33

* The names refer to the Knickerbocker Cement Co., the Houston Cement Co., and to Harvey Randolph Durbin, the patentee.

By the addition of the extra amount of lime, the ratio of the calcium silicates is changed from: 5 tricalcium silicate and 4 dicalcium

[13] *Ind. Eng. Chem.*, **18**, 554 (1926).

licate, to: 8 tricalcium silicate and 1 dicalcium silicate. Uncombined, ee lime in the finished product is detrimental, as it is in any cement, ld it is studiously avoided. The H.E.S. cement is not only quick-:tting, but also has exceptionally high strength, and is "volume-mstant."

LIME

Lime, more properly called quicklime, is the oxide of calcium, CaO, nd is obtained by driving the carbon dioxide out of limestone, a slightly npure calcium carbonate, $CaCO_3$, by means of heat and a current of fire ases. The reaction $CaCO_3 \rightleftarrows CaO + CO_2$ is reversible; it runs to the ght completely if the carbon dioxide is removed; this the fire gases do, ence closed retorts are not likely to be found in the lime industry.
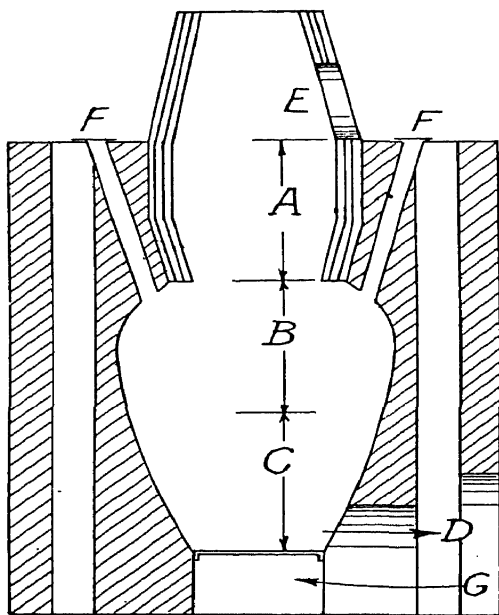
FIGURE 51.—A vertical lime kiln, with continuous operation; *A*, warming zone; *B*, combustion zone; *C*, cooling zone; *D*, discharge for lime; *E*, charging hole for limestone; *F*, fuel canals; *G*, air entry.

The modern limestone kiln is operated continuously; in isolated disricts with small lime requirements, the cruder kiln of early days may till be used to advantage. Like all intermittent operations involving ieat, the intermittent lime kiln wastes heat; at each charge, the cold :iln must itself be heated. In the kiln with continuous operation, this vaste is avoided; the kiln is always hot. The modern kiln is usually rertical. The fuel may be mixed with the limestone in alternate ayers, fed in from the top; or the coal may be burned in separate fire-ilaces, whose hot gases pass into the kiln proper, while the ashes remain in the grate bars and do not contaminate the product, so that a purer

lime results. The temperature in a lime kiln is more moderate than in the cement furnace; 1000° C. (1832° F.) is sufficient.

The carbon dioxide passing out is usually wasted; in special cases, such as the lime kilns in the ammonia soda plants, a hooded kiln is used and its gas drawn by a pump from the top. A kiln with continuous operation and with fuel and limestone mixed is shown in Figure 51. The limestone, in lumps free from fines (screened), is served from the upper platform at the top of the kiln. The coal is fed in by separate channels which bring it to the main part of the kiln; here it meets warmed lime, and the combustion proceeds briskly, while at the same time the limestone loses its gas. As the charge continues on its way downward, now well burnt, it is swept by the incoming air, and thereby cooled, so that when drawn off at the base, either periodically, by hand, or continuously, by conveyors, it is nearly cold. This is desirable not only because the lime may then be handled at once, but because the heat is regenerated, and not wasted. Such regeneration of the heat is almost complete in the kiln shown, and this is reflected in the low fuel consumption, which is about 12 per cent of the weight of the product; the theoretical consumption is 11.2 per cent. A kiln 40 feet high and 16 feet at the widest part delivers 15 to 20 tons of lime.

During the burning the charge shrinks. If the limestone contains clay impurities, it fuses slightly, and is inferior, sometimes useless; it is then said to be "dead burnt." A reasonably pure lime when treated with a limited amount of water will heat, swell, and form a powder consisting mainly of calcium hydrate or hydrated lime; if made up with boiling water it will form a thick cream, leaving a few unattacked stones. Nearly all limes contain some grit, mainly silica sand.

The lime made in contact with the coal is slightly discolored, and contains such ash as the coal contained. This is usually not a serious matter; if it must be avoided, outside fireplaces are used, forming part of the kiln, and sending their fire gases into the shaft. Still another method is to burn the coal in a gas producer and to send the gas into the kiln; several kilns may receive gas from one producer.[14] Aside from the stationary kilns described above, rotary kilns similar to the Portland cement kilns, but shorter, are also used.

Lime as quicklime is used for mortar, a mixture of lime, sand, and water; it sets due to the evaporation of water and the absorption of carbon dioxide from the air. Mortar has been largely displaced by Portland cement, but seven-tenths of the lime made is still used for structural purposes, either as mortar, or mixed with cement or plaster. Lime is used in the chemical industries,[15] such as the ammonia soda, gas purification, paper making, and tanning. Hydrated lime is used to make sand bricks, and as a fertilizer; it is also one of the raw materials for bleaching powder.

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[14] "Burning lime in a gas-fired continuous kiln," W. D. Mount, *Chem. Met. Eng.*, **20**, 428 (1919).

[15] A full list of the uses for lime will be found in *Ind. Eng. Chem.*, **10**, 216 (1918).

TABLE 19.—*Production of Lime in the United States for 1935.*

	Tons	Price per ton
Quicklime	1,414,650	$6.91
Hydrated lime	837,876	8.45
Agricultural lime	223,819	6.03

GYPSUM PLASTER

Gypsum plaster is made by removing most of the water of crystallization from gypsum, $CaSO_4 . 2H_2O$, by gentle heat; the plaster so produced when mixed with water may be spread and shaped, and in a few hours it sets to a hard mass. Gypsum plaster is almost universally used for coating the inner walls of dwellings. It is often called plaster paris, because huge deposits of gypsum are found in Paris and in its neighborhood, and these were the first to be worked.[16]

While limestone is found exposed or covered by an overburden easily stripped off, permitting open pit operations, gypsum occurs at greater depths generally, and shaft operations are the rule. It may be said also that limestone is far more common than workable gypsum deposits. This is due partly to the fact that only the rock with the composition $CaSO_4 . 2H_2O$ may be used; if it contains less water, calcining it does not produce a material which sets with water. A seam 3 feet in thickness is considered valuable, if it has a reasonable extent; the deposits near Buffalo have such thickness and have an area roughly of 1 square mile.[17] The depth at which they lie averages 80 feet. The method of mining is by entries, and "rooms," 250 feet deep and 25 feet wide.[18] Holes are drilled by electric augurs; 20 per cent dynamite is used for blasting, and is exploded by a fuse. The broken rock is loaded into the mine cars which are pulled by an electric (D. C.) locomotive to the shaft or incline. Gypsum rock is nearly white, and has large crystals; it is a soft rock. Gypsum mines do not require artificial ventilation.

The mine cars are dumped into a gyratory crusher[19] with a pot 11 feet deep; the product is elevated to a rotary screen, which separates the fines from the lumps, about egg size. The fines are shipped to Portland cement plants.[20] The lumps are fed to a rotary drier, a horizontal steel cylinder 30 feet long, with internal firing; the rock is passed through so fast that it attains a temperature of only 150° F. (65° C.). The dried rock is more easily crushed further and pulverized; the devices used are a swing-hammer mill[19] followed by inclined flat screens; the material which passes through the screen is sent to a Raymond suction mill,[19] the tailings (on the screen) are returned to the swing-hammer mill. The pulverized material from the Raymond mill is sent to the calciners,

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[16] It was the study of gypsum plasters which led the French chemist, Le Chatelier, to his investigation of the constitution of Portland cement.

[17] Akron, Scottsville, Oakfield, and Clarence, New York.

[18] *Compare* coal mining in Chapter 12.

[19] Chapter 44.

[20] *See* the first part of this chapter.

upright cylindrical vessels with slow-moving agitators, and several horizontal flues through which fire gases pass. The fine powder remains in the calciner 1 hour; the temperature is about 350° F. (177° C.); three-quarters of the water of crystallization is removed, not more. After calcining, the powder is white; it is discharged through a door at the base of the calciner which leads to conveyors; these bring the material to the storage house.

Calcined gypsum is made into wall plaster by the addition of asbestos, hair, shavings, sweepings from packing houses, and dextrin, according to specifications. Without addition, it is plaster paris. Considerable amounts are used at the mill itself to make plaster boards,[21] which may then be placed on the walls of dwellings with little labor, and by any one unskilled in plastering. The manufacture of these plaster boards is largely automatic. The calcined rock is mixed with 8 per cent (by weight) of selected sawdust on a conveyor which passes into a shallow tank where it takes up the right amount of water for setting. The wet mass is dumped on a sheet of paper, leveled, and covered by a second sheet; the edges are folded over, and the sheet pulled continuously toward the knife; by the time it reaches it, 12 minutes have elapsed. The board may now be handled, although it is not dry. The knife cuts it in appropriate lengths; these are dried in tunnels, by a stream of warm air, while suspended vertically to avoid warping.

Gypsum plaster is valuable for making casts; on setting, there is an increase in volume of 1 per cent and as a result, the casts are sharp. For temporary buildings imitating famous examples of architecture, such as for the International Exposition in Paris (1937), gypsum plaster is used in vast quantities.

An artificial gypsum has been mentioned in Chapter 7.

In 1935, the gypsum mined in the United States amounted to 1,937,500 tons; the least valuable is the uncalcined rock sold to cement mills, valued at $1.75 a ton. Calcined gypsum, in plaster form, brought $9.57 a ton; while wall board was worth $35.35 a ton. The prices stated are for 1934.

Magnesium Oxychloride Cements

This name is given to cements made by adding a strong solution of magnesium chloride to magnesium oxide, usually called calcined magnesia. A filler such as small stones, wood flour, cork, is mixed into the paste. After a short time the paste sets to a hard mass approximating Portland cement in strength. The proportions of solution and magnesium oxide must be properly chosen and strictly observed. The cement after setting takes a high polish; it is used only for interior work such as floors in hospitals and public buildings.

Sorel cement is a magnesium oxychloride cement.

Examples: "Best Wall," "Sheet Rock."

OTHER PATENT

U. S. Patent 2,069,164, rotary kiln.

PROBLEMS

1. Since three-quarters of the water of crystallization of the gypsum is removed during calcination, show that the finished material retains 6.1 per cent water.

2. A lime kiln delivers 27 tons of lime per day; how much limestone must be fed in, assuming both substances to be pure and the burning perfect?

3. The amount of fuel per barrel of finished Portland cement is given in the text (an average). For a furnace producing 215 tons of cement per day, how many tons of coal must be provided?

4. A Portland cement contains its calcium silicates in the proportions of 5 tricalcium silicate molecules to 4 dicalcium silicate. Compute the absolute amount on the basis of 23.46 per cent SiO_2 in the Portland cement. How much lime (CaO) must be added to change the ratio of the calcium silicates to the new one, namely 8 molecules of tricalcium silicates to 1 of dicalcium silicate? How much limestone is required, if it contains 95 per cent $CaCO_3$? All the lime added will react with dicalcium silicate. What is the limestone quantity to be added in terms of the original Portland cement?

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"Liberation of heat during the hydration of concrete," N. Davey, *J. Soc. Chem. Ind.*, 53, 343T (1934).

"The rate of hydration of Portland cement and its relation to the rate of development of strength," F. M. Lea and F. E. Jones, *J. Soc. Chem. Ind.*, 54, 63T (1935).

The great importance of ceramics to the chemical industries is evident when it is pointed out that the steel shells of the Portland cement furnace, of the Bessemer steel converter, of the sulfite pulp digester, of the gas producer and water-gas generator are lined with bricks; in addition, the fire box under boilers, the reverberatory furnaces for varied purposes, and the tank furnaces for glass depend for their proper construction upon ceramics. These are only a few examples and leave out of reckoning the building bricks and stoneware.

Chapter 10

Ceramic Industries*

Ceramics primarily comprises the several arts of shaping wet clay, generally with an admixed material, but in such amounts that the clay remains the important constituent; the shaping is followed by drying and firing in kilns. Ceramics also includes products in which the clay is present in small amounts, so that it acts merely as a bond; this inclusion extends the range of ceramics considerably. A survey would indicate that the following products are included: Common (red) building bricks, mainly clay containing iron, rather fusible; fire-resisting bricks (firebricks), the more resistant the nearer their composition approaches aluminum silicate, $Al_2O_3 . 2SiO_2 . 2H_2O$, the pure clay substance, infusible at the highest temperature of a coal fire (1400° C., 2552° F.); basic bricks; acid bricks—for example, silica bricks, in which the lime bond is 2 per cent of the total; grinding wheels of various abrasives, with clay as the bonding material; crucibles; pottery, including stoneware and porcelain, in which the proportion of clay is high, so that its plastic property becomes the property of the whole mixture; finally, porcelain enamel, which contains a small amount of clay. Sand bricks bonded by lime do not belong under ceramics, but will be treated briefly after the common bricks.

Clays differ in many particulars, especially in their plasticity, which in turn depends upon their content of admixed organic matter, upon their state of hydration, and upon the fineness of the subdivision of the particles. A plastic clay is called a fat clay; a less plastic one a lean clay. Plasticity is really the resultant of two separate properties: deformability, which allows shaping, and tenacity, which resists tearing. In drying and baking, the clay body (for certain clays, not for all) contracts so much that the article would develop cracks and be useless; the shrinkage is reduced by the admixture of a non-shrinking material such as clay itself which has been calcined, for calcined clay loses its power to contract and at the same time its plasticity. Another non-shrinking admixture which is used is ground flint (SiO_2). In general, the lower the proportion of clay the weaker the article; the more plastic the clay, the harder and stronger the article after drying and baking, and the greater

the shrinkage. Clays are included in the substances studied from the standpoint of the colloidal state (colloid chemistry).

Another property of clays which is of great moment is their fusibility, which differs according to their impurities, geological history, and substances purposely admixed. Clays fuse less, the greater their content of aluminum silicate $Al_2O_3 . 2SiO_2 . 2H_2O$; the addition of metallic oxides renders them more fusible. The addition of silica within certain limits also makes clay more fusible.

Clays in general have been formed from rock decomposition by various agencies through time. If the clay remains at the original location, it is a primary clay, usually white, and with a low content of iron so that it "burns" white; it is called kaolin or *china clay*. It might be said that kaolins are the product of the weathering of feldspar, either potash feldspar $K_2O . Al_2O_3 . 6SiO_2$, or soda feldspar, $Na_2O . Al_2O_3 . 6SiO_2$; the alkali is washed away. They would then be termed primary clays, and this is true enough if the statement be qualified by adding that some kaolins such as the Florida and Georgia kaolins are transported, hence of secondary origin. If, in the course of geological changes, the clay has been transported (by water, glacier, or wind) to another location, it is a secondary clay [1]; it has lost the undecomposed, coarse particles of feldspar which remain in certain primary clays of that origin, but it now contains limestone powder, hydrated oxide mud, and organic impurities, in varying amounts. In general most of the clays other than white clays are of secondary origin, but there are exceptions here too, as for example the red burning clays of Washington and Oregon, which have been formed by the weathering of basalt rock. The purer deposits of the secondary clays are more plastic than china clay, and are used under the name of *ball clays*.

TABLE 20.—*Analysis of China Clay and Secondary Clay.*

	China clay* washed free from admixed quartz	Secondary clay**	Kaolin $Al_2O_3 . 2SiO_2 . 2H_2O$
Silica SiO_2	47.5%	50.33%	46.5%
Alumina Al_2O_3	37.4	27.06	39.5
Iron oxide Fe_2O_3 .... }	0.8	2.29	
Iron oxide FeO .... }		2.62	
Lime CaO	trace	1.22	
Magnesia MgO	0	3.34	
Soda Na_2O .... }	1.1	1.78	
Potassium oxide K_2O .... }		4.40	
Water H_2O	12.48	6.66†	14.0

* "The clays and clay industries of Connecticut," by G. F. Loughlin, State of Conn., State Geological and Natural History Survey, Hartford (1905), p. 47.
** *Ibid.*, p. 59.
† Includes all loss on ignition, organic matter as well as water.

The plasticity of a clay may be increased by aging, that is, storing it damp; the process is partly one of hydration accompanied by gelation, and partly a bacterial action which has as one of its results the further subdivision of the particles. Whiteware bodies are aged after filter

[1] River deposits are called fluviatile or alluvial, lake deposits lacustrine, and sea deposits marine.

pressing by stacking the cakes one on top of the other in damp cellars or bins. Clays are also washed for certain uses, and levigated in order to free them from coarse particles.

The analytical figures for a high-grade china clay and a secondary clay are given in Table 20.

The Manufacture of Whiteware

Whiteware such as dinnerware, electrical porcelain, chemical porcelain, floor and wall tile, is generally made from a mixture of clays and other materials. Usually these consist of kaolins [2] (china clay), ball clays, feldspar, and flint. The proportions of each of these depends upon the uses to which the ware will be put. Other materials which may be added are talc (steatite), whiting ($CaCO_3$), or magnesite ($MgCO_3$).

Dinnerware represents a large portion of the whiteware field; it is made by one of two methods, which are also the ones used in all the other branches of porcelain manufacture; these are casting and jiggering.

Making the Slip. The proper amounts of the clays are weighed out and stirred in a blunger with water which may (but need not) contain electrolytes to disperse the clays until most of the lumps are broken up. The other materials such as feldspar, flint, are then added and the whole stirred until homogeneous. The "slip," as the mixture is now called, is of a thin creamy consistency and flows readily. It is allowed to run from the blunger through a vibrating screen, which removes bits of wood and metal, and lignite, and thence over a magnetic separator to remove iron particles which would stain the fired ware.

Clay Body is Filtered and Aged. From here, the slip flows to filter presses [3] where it is separated from the water and forms cakes with 10 to 30 per cent of water. The cakes are stored in damp cellars where they are allowed to age. The aging process improves the plastic properties of the clay body and insure even distribution of moisture in the mass.

From this point on the body is made into ware either by the casting process or the jiggering process.

Casting Process. The clay body from the aging bins is placed in blungers with about 35 per cent water and the proper amount of electrolytes, usually a mixture of equal parts of sodium silicate and sodium carbonate, in amount sufficient to give a fraction of one per cent. The clay body and water are thoroughly mixed, again screened [lawned] and run over a magnetic separator. The mixture now has the consistency of a not too heavy cream, and flows readily; it is now termed the "casting slip" and is ready for use.

Casting Slip run into Molds. Plaster paris molds having for the inside of the form, the dimension and lines of the outside of the object to be

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[2] Kaolin is refractory, that is, it does not soften below 1700° C. [3092° F.] so that it is infusible at the kiln temperature; ball clay to hold water; flint for whiteness, rigidity, and to reduce shrinkage; feldspar as the flux or binder.

[3] Chapter 42.

cast, are at hand. They are filled with slip, and let stand for 15 to 30 minutes, and then the excess slip poured out. The plaster paris absorbs the water, and the clay body is left as a lining of the mold walls, exactly reproducing them. After pouring off the excess slip, the mold is allowed to drain, and is set for a period of 20 to 45 minutes in a warm place. At the end of this time the clay lining has set and shrunk sufficiently to allow its removal from the mold; the latter is used over again.

The cast ware is then trimmed and dried in hot air driers, after which it is fired. In some plants, and for some wares, a glaze coating is applied to the dried ware and both body and glaze are fired together. In general, however, a separate firing is given before and after glazing known in the first case as the bisque firing, and in the second case the glost fire.

Jiggering Process for Tableware. In making ware by "jiggering" or "jollying," the clay body from the storage bins is fed into a pug mill and tempered with enough water to give a stiff-mud consistency. From the pug mill it is forced by augurs through a die in the form of a cylinder or "wad."

The "wads" are ready for use and are distributed to the jiggermen. The jigger consists of a rotating unit carrying a mold which will form one face of the ware while the tool forms the other face. For tea cups, which are made without handles, because these are fastened on later, the

FIGURE 52.—Cross-section through plaster paris form for shaping clay cup.

mold forms the outside of the cup, and the tool the inside. For plates, the inner surface (later, the upper) is formed by the mold, and the bottom surface by the tool. Oval platters are made on a jigger having eccentric motion.

To make each object, a piece from the wad of just the right size is thrown on the center of the rotating mold and the tool brought down on it, spreading it over the mold and cutting away the excess clay. The tool is of metal and has a profile shape of the form desired on the surface it makes. During this operation the jiggerman keeps the clay-tool interface lubricated with water. The formed ware is placed with the mold in the drier. After drying, the ware is taken off and treated like the cast ware. The dry molds are returned to the jigger.

This process is much more rapid than the casting process and is used wherever the shape of the object does not prohibit it. It can be used for all simple shapes which contain no bulges or reverse curves.

The Saggers. In order to protect the ware from soot and dust during the firing, it is packed in clay boxes called saggers. Each box is open; they are piled on each other from the base of the kiln to the top, and the second box closes the first. The saggers are made of various shapes and heights, to fit the ware. For example, one sagger box can hold 4 piles of 20 plates each; the lowest plate rests on a thick form, the setter,

which is used over and over; it prevents the deformation of the lowest plate when it softens. The other plates are supported each by the next lower one, separated by flint granules, known as "bitstones."

The making of new saggers is a constant operation. The materials are broken saggers ground to a coarse powder, new clay, untreated in any way, and water. The mass is mixed in a pug mill, which cuts and mixes the dough-like mass, and discharges it into an extrusion machine which forces it out in the shape of a loaf of bread. This is cut in lengths of 16 inches or so, and one length is placed under a press which forms the saggers at one stroke between the descending die and a steel box. After firing, the scaggers are ready to be used, and serve several times; when cracks in the side develop, they must be discarded.

FIGURE 53.—Sketch of a typical pottery kiln. The ware is placed in saggers and these are set in the kiln in vertical rows called "bungs." The fire gases are directed upward by the bag walls in part, while another part is drawn to the center of the kiln by flues and ascends through the ware.
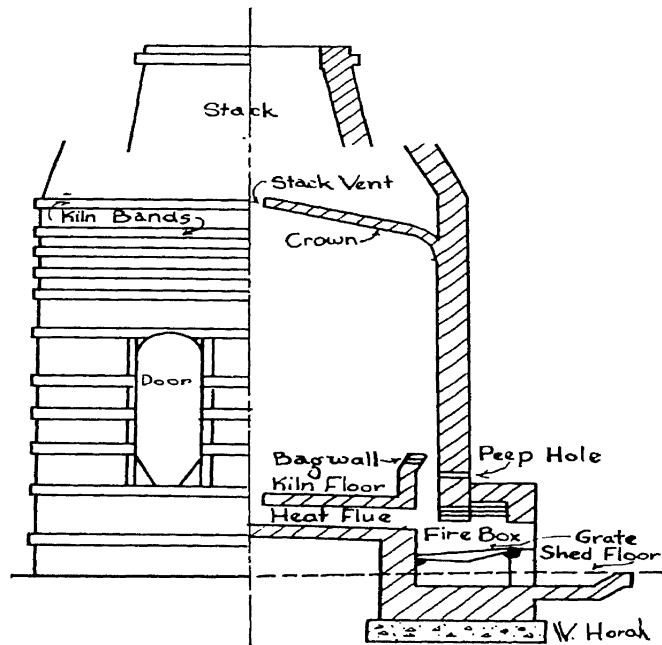
The Pottery Kiln. The ware packed in the saggers is ready for the firing, which is done in one of a number of kilns, circular in cross-section, built of bricks, about 12 feet in diameter and 12 to 14 feet high inside. The kiln is built of common bricks outside, fire-bricks inside, and is surmounted by a stack. Each kiln has 6 to 8 small fireplaces or so at the base, whose fire gases enter the inner chamber at circumferential openings, and in addition at one central opening, in the floor. To provide room for the fireplaces and necessary channels, the floor of the kiln is about 4 feet above the room floor (ground). The saggers are so arranged in the firing chamber that 5 "quarters" result, and within these quarters, the circulation of the fire gases may be regulated by means of empty saggers with

suitable sections knocked off. A column of saggers set one on top of the other in the kiln is called a "bung." The fire gases leave the kiln through a stack vent in the crown and from there to the stack proper, which surmounts the structure. By these means, the temperature may be so controlled that there is a difference of 15° F. (8° C.) at the most between the top and the bottom. The heat is raised very gradually. The temperature at various plants is observed by means of pyrometric cones (or Orton cones)[4] sighted through peepholes at various levels. The time of actual firing is about 66 hours; including cooling, unloading ("drawing"), and reloading, the cycle is 1 week. The maximum temperature is 2500° F. (1371° C.). At each packing the kiln is filled to capacity, about 2200 dozen pieces. The ware shrinks 10 per cent. The fuel is coal, gas, or oil, with coal the most common, although gas and oil are not rare, since the ware is high enough in price to allow the use of the dearer fuel.

The product from this first firing is the biscuit ware, strong, nonporous, and white; the second or gloss firing is at a lower temperature and shorter. There are a few potteries which fire low at the first firing and high at the second.

A modified procedure has recently been developed which will have far-reaching, beneficial effects. The air remaining in the plastic clay, as it leaves the pug mills, is removed by the application of a vacuum. It is found that such de-aired products are stronger for a given thickness of wall than the untreated ware, or as strong with a smaller wall thickness. Some clays which previously could not be used give satisfactory results when de-aired. The same wall thickness, with firing at a lower temperature than previously, gives a ware as strong.[5]

Decorating and Glazing. For under-glaze decorations, the biscuit is brushed with shellac, and the pattern transferred to it by means of decalcomania paper. The pigments are so selected that the color obtained after firing is the desired one; the first color from the transfer paper is immaterial. Very elaborate designs covering the whole plate in some cases may be applied by means of decalcomania paper. Hand painting is also practiced, and a combination of decalcomania and hand painting. The decalcomania paper may be made in the pottery itself, from an etched plate coated by the proper pigments, and applied to a strong but thin paper first treated with a soap solution.

The decorated pieces are passed into a suspension of the glaze; they retain enough to cover them. Next they are dried and packed in saggers again, but this time they must not touch; they rest on three pegs set in the wall of the sagger.[6] The saggers are fired at a lower temperature for 30 hours only. The glaze is more fusible than the biscuit, and no deformation takes place. Over-glaze decoration is less durable.

The glaze must be transparent for underglaze decoration; it may be

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[4] Chapter 46.

[5] "The effect of de-airing stiff-mud bodies for clay products manufacture," by J. O. Everhart, C. R. Austin, and W. C. Rueckel, _Ohio State University Studies, Engineering Series, Bull._ **74** (1932); in cooperation with the Bonnot Co., Canton, Ohio.

[6] The marks of the three pegs may be seen on the under side of almost any plate.

opaque for overglaze decoration; it must have the same coefficient of expansion when heated as the under body, so that it shall not "craze" nor peel off. One formula includes sodium oxide, borax. zinc oxide, silica, tin oxide, calcium carbonate, and lead oxide; it produces an easily fused, non-transparent, white glaze.

There are various kinds of tableware bodies; the more important ones are real porcelain, strong and non-porous (red ink makes a slight stain); semi-porcelain, less strong, somewhat porous (red ink makes a deep stain).

Stoneware is made from clays not selected for color, although in some cases the color is pleasing; it is fired at a temperature approaching that at which porcelain is fired. The ware is not packed in saggers, and the glaze is applied by means of salt, introduced at the top of the hot kiln; the salt melts and attacks the surface of the ware just enough to make it run. Stoneware is cheaper than porcelain except in a few cases when for artistic merit the ware brings as much as porcelain. Earthenware has a porous body; it is baked at moderate heat, insufficient to cause complete vitrification; if the ware is to be water tight, it must be glazed. There are many products which occupy intermediate places so that a classification is difficult. Chemical stoneware is generally brown in color, and fired without saggers, but it is made with great care. Certain pieces such as the Cellarius vessel [7] have surprisingly thin walls, so that cooling may be rapid, yet they are strong; other pieces are used chiefly for storage of acids, and are as large as 6 feet in height; the walls are then made thicker.

Electrical insulators of the umbrella type, for high tension currents, are made of a clay mixture very similar to the kind used for fine tableware. A large unit is about 10 inches across and 6 inches high; it is shaped in a mold for its one side, and with a tool on the jigger table for the other. The units are dried, packed in saggers, loaded on kiln cars, and fired in a tunnel kiln, one car moving out at the south side, let us say, as the new enters at the north side. The firing (oil) is in the middle; the fire gases sweep north, preheating the incoming kiln car. The combustion air enters at the south point, sweeps over the fired ware, cooling it, and reclaiming the heat. The insulator units are glazed. They are tested for resistance to high voltage current, as well as in a number of other ways. Twenty units set up one in the other offer enough resistance to prevent a million-volt current from passing.

Iridescent ware (lustre ware) is produced by exposing the hot ware to the vapors of stannous chloride or ferric chloride. Iridescence combined with color is produced by applying silver sulfide and clay mixed, and exposing to a smoky (reducing) flame.

Gold gives its characteristic color over the glaze, old rose under the glaze. Cobalt oxide applied under glaze produces a beautiful deep blue, due to the formation of the blue silicate; similarly, chromium oxide burns to a green; uranium oxide to black.

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[7] Chapter 3.

BUILDING BRICKS

The familiar red brick is made from a secondary clay containing in the neighborhood of 4 per cent iron oxide as a natural impurity. If the clay is rich, that is, relatively pure, sand, crushed rock, or cinders must be added [8]; a less pure clay, a "mild" clay, which contains gravel or sand, is preferable. For the cheapest good bricks, the dry material must pass through 8-mesh screen; for finer grades, a 20-mesh screen. The density of the brick depends mainly upon the method of working; a wire-cut brick, not re-pressed, would be the lightest; on placing it in a mold and pressing it by a screw-operated die, it becomes denser, as well as more accurate; power pressing will raise the density still further.

Stiff-mud Process for Heavy Clay Products. This process is widely used for making building brick, tile, paving brick, some terra cotta, conduit, drain tile, and for some types of firebrick. A variation of the process here described is used for making most sewer pipe.

The clay as it comes from the pit or storage bins is ground in dry pans and carried to a pug mill, where it is tempered with the proper amount of water to give a stiff mud-like consistency. From the pug mill it is forced by an auger screw through a steel die of the shape and size desired for the finished ware. The clay issues from the die head as a continuous column. A few feet from the die head, a cutter, generally automatic, consisting of piano wires set at proper distances on a jig (movable frame), cuts the column into the right lengths. The cut raw ware continues on a belt conveyor from which it is picked and set on a drier car. Full cars of bricks, with 1,000 to 2,000 bricks per car, are pushed into driers and left to dry according to a predetermined schedule for the particular clay used. From the driers, the cars are taken to the kiln yard, the dry ware taken off and set in the kiln, usually of the down draft type, for firing.

The Round Down-draft Kiln. This kiln is 40 feet in diameter and 19 feet from the floor to the top of the crown; it has eight fire boxes around its circumference. The heat and combustion gases from the fire boxes are directed upward toward the crown and are reflected by the crown downward through the ware; the gases pass through slots in the floor into the collecting flues and center well hole, and finally through the main flue to the stack. The firing temperature varies considerably; in the case of a dense red brick, to give an example, the maximum temperature will lie between 1470° and 1650° F. [800° to 900° C.].

By skillful setting of the ware and skillful firing, the temperature distribution may be made uniform throughout. This type of kiln is periodic in operation; they are fired by coal, oil, or gas, but mostly by coal.

After firing, the bricks are sorted; those with perfect shape and correct dimensions are No. 1 bricks; less perfect ones are grouped together as seconds; insufficiently burnt ones are added to the new charges. The price of wire-cut red bricks, of first quality, is about $10 a thousand.

[8] The rich clay without addition would shrink and crack badly when fired.

Sand-lime Bricks. In districts without clay resources, bricks which approximate in strength the common red bricks are made from sand, or crushed sandstone (by-product of a sandstone quarry) mixed with about 8 per cent of carefully hydrated lime.

Quicklime is treated with the proper amount of water

$$CaO + H_2O = Ca(OH)_2$$
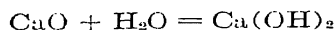
in an iron box; there is produced a light fluffy powder which is screened and stored in silos in order to insure complete hydration. It is mixed with sand and enough water to give a dough which may be shaped in presses. The new bricks are loaded on small trucks and pushed into
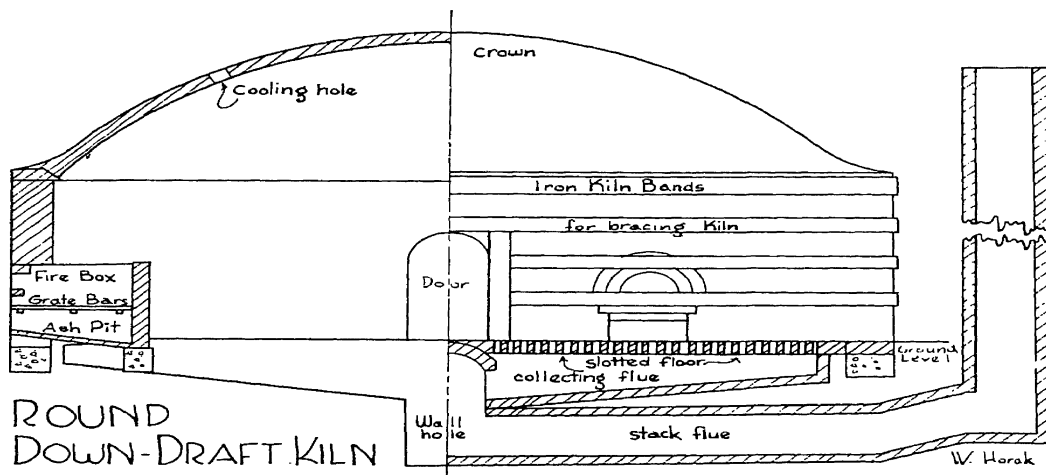
FIGURE 54.—The round down-draft kiln, suitable for firing heavy clay products. (See text.)

autoclaves, where they are subjected to the action of steam at **125** pounds pressure; this operation is called "curing" and corresponds to the firing of the red bricks. Usually bricks are shaped in the daytime and cured over night. The bond between the sand particles is monocalcium silicate.[9] The price of sand-lime bricks is about the same as that of common bricks.

FIRE-BRICKS

Fire-bricks are the material for the construction of open-hearth steel furnaces, for the iron and other blast furnaces and stoves, for cupolas, calciners, and many other chemical engineering apparatus; they serve to line fireplaces, furnaces, and to fill regenerators. The materials are a fireclay made even less plastic than it normally is by a preliminary firing at high temperature followed by crushing and known as "grog"; and a

[9] "Manufacture and properties of sand-lime brick," W. E. Emley, *Bureau Standards Tech. Paper*, **85**, Washington (1917).

smaller proportion of a more plastic clay to furnish the bond. The firing is done at a temperature of 2200° F. (1200° C.), or somewhat higher. The burnt brick is cream colored, or light buff; it is generally softer than the common brick, but may also be as hard or even harder. Fire-bricks bring about $40 per thousand.

There are many kinds of refractories; the primary objective is to produce a shape or brick which will resist the attack of metals, slags or glass at high temperatures without appreciable distortion or softening. Another objective is to produce bricks or shapes for high temperature insulation; such bricks do not resist abrasion and slagging. They are used as a backing to a first course of slag-resisting bricks. The insulating bricks are generally very light in weight; "cork brick" is an example.

The nature of the raw materials will depend upon the intended use; silica will be selected for bricks which must be acid resisting, but silica bricks are also used for heat conducting, in the by-product coke oven for instance. Basic bricks, which resist basic charges, are made of magnesia, bonded only by water, under great pressure, or by bauxite or alumina. There are also neutral bricks, such as chromite, graphite, silicon carbide. In metallurgy, the nature of the slag determines the class of refractory to be used; thus a siliceous slag requires an acid refractory. For crucibles which must conduct heat as well as resist high temperature, natural graphite [10] bonded with 30 per cent clay and some water glass is largely used. Silicon carbide bonded with lime serves for muffles and electric furnace linings; clay-bonded silicon carbide is the general choice for high heat-conductivity brick; with graphite in addition, the mass becomes sufficiently elastic to form crucibles. An excellent high conductivity crucible is made from silicon carbide [11] and tar; the carbon residue from the latter becomes the bond and is prevented from oxidizing during use by a glaze. Clay pots are used in the glass houses; they are purchased unburnt by the glass maker, who must burn them in his own furnaces.[12]

The highest grade silica bricks are made of quartzite or ganister, and bonded by 2 per cent lime; they are generally heated twice, because they expand when heated (fire-clay bricks shrink), and it is desirable that the expansion be complete before the wall or lining is built. The expansion is due to the change of quartz into cristobalite and tridymite, which are less dense forms of silica.

Much harm can be done by too rapid heating of the bricks in the process of manufacture; and the gradual cooling is just as important, for too rapid cooling causes strain and weakens the brick.

For some years, refractories have been produced in the electric furnace.[13] (Compare next chapter).

The fireclay refractories, priced at $35 to $45 a thousand [with shapes

[10] Formerly Ceylon graphite; now largely Madagascar graphite.
[11] U. S. Patent 1.356.939.
[12] Chapter 11.
[13] Fred W. Schroeder, *Ind. Eng. Chem.*, **23**, 124 (1931).

computed to the standard $9'' \times 4\frac{1}{2}'' \times 2\frac{1}{4}''$ brick], make up 75 per cent of all refractories; their distribution is 35 per cent to boiler linings, locomotives; 20 per cent to open hearth steel furnaces; 10 per cent to heat treating furnaces and the like; 4 per cent to the glass industry; 4 per cent to the ceramic industry. As to composition, there are four types, a high silica (75 per cent), a high alumina (28 per cent), a high flint fireclay (40 per cent silica, 43 per cent alumina), and a plastic fireclay (52 per cent silica, 33 per cent alumina).

Refractories are tested for the temperature of deformation under load, linear shrinkage on heating, resistance to spalling on repeated heating and sudden cooling, and on resistance to three types of slag.

A few further particulars will be found in chapter 45.

Vitrified Enamel or Porcelain Enamel

"Vitreous enamels [14] or porcelain enamels are fused silicate coatings applied to metal (usually cast iron or sheet steel).

"The first step in all types of vitreous enameling is the making of the 'frit.' Proper proportions of raw materials such as feldspar, borax, soda ash, silica, fluorspar, cryolite, sodium nitrate and the like are thoroughly mixed and then fused in a smelting furnace. The melt is drawn off into water and the resulting friable product is termed 'frit.'

"The application of the enamel is accomplished by two general methods, the wet and dry process. In the former method the frit is ground in a pebble mill in the presence of water and clay to produce a workable suspension, or 'slip.' Opacifiers and coloring oxides are also added in the milling.

"The ware to be enameled by the wet process, after proper fabrication and cleaning, is coated by dipping it in the milled enamel followed by draining off the excess, or by spraying the slip onto the ware. In either case the enamel coating is dried and then fused in an enameling furnace. One or more coats are thus applied as may be required. The coat applied directly on the metal is usually of a special nature [15] to promote a firm adherence, while subsequent coats develop the desired color and texture.

"For application by the dry process, dried frit is ground to a fine powder in a dry mill, with the addition of the proper coloring oxides and opacifiers. The piece to be enameled receives a first coat by the wet process. The burnt first coat is not allowed to cool, however, but while the article is still hot the dry ground enamel powder is applied by means of a sieve. The piece of ware is then replaced in the furnace and the coat fused. Two or more such applications are usually required to produce the desired results.

[14] The quoted portion is the statement prepared especially for this edition by Mr. Emerson P. Poste, Consulting Chemical Engineer, Chattanooga, Tenn.

[15] A ground coat is applied to cast iron and sheet iron, and fired; it must contain cobalt to promote the adherence to the metal surface; it is then dipped or sprayed with the cover coat, and fired once more (firing time 3 to 7 minutes). E. R. R.

Pyrometric Cones (Originally Known as Seger Cones)

Table of Fusing Points

Category	Cone Number	When fired slowly 20° C. per hour °Cent.	°Fahr.	When fired rapidly 150° C. per hour °Cent.	°Fahr.
Decoration	022	585	1085	605	1121
Decoration	021	595	1103	615	1139
Decoration	020	625	1157	650	1202
Decoration	019	630	1166	660	1220
Decoration	018	670	1238	720	1328
Decoration	017	720	1328	770	1418
Decoration	016	735	1355	795	1463
Decoration	015	770	1418	805	1481
	014	795	1463	830	1526
	013	825	1517	860	1580
	012	840	1544	875	1607
	011	875	1607	905	1661
	010	890	1634	895	1643
	09	930	1706	930	1706
	08	945	1733	950	1742
	07	975	1787	990	1814
Heavy Clay Products	06	1005	1841	1015	1859
Heavy Clay Products	05	1030	1886	1040	1904
Heavy Clay Products	04	1050	1922	1060	1910
Art Pottery	03	1080	1976	1115	2039
Art Pottery	02	1095	2003	1125	2057
Art Pottery	01	1110	2030	1145	2093
Art Pottery	1	1125	2057	1160	2120
Art Pottery	2	1135	2075	1165	2129
Art Pottery	3	1145	2093	1170	2138
Whiteware	4	1165	2129	1190	2174
Whiteware	5	1180	2156	1205	2201
Whiteware	6	1190	2174	1230	2246
Whiteware	7	1210	2210	1250	2282
Whiteware	8	1225	2237	1260	2300
Whiteware	9	1250	2282	1285	2345

Category	Cone Number	When fired slowly 20° C. per hour °Cent.	°Fahr.	When fired rapidly 150° C. per hour °Cent.	°Fahr.
Electrical Porcelain	10	1260	2300	1305	2381
Electrical Porcelain	11	1285	2345	1325	2417
Electrical Porcelain	12	1310	2390	1335	2435
Electrical Porcelain	13	1350	2462	1350	2462
Electrical Porcelain	14	1390	2534	1400	2552
	15	1410	2570	1435	2615
	16	1450	2642	1465	2669
	17	1465	2669	1475	2687
Refractories	18	1485	2705	1490	2714
Refractories	19	1515	2759	1520	2768
Refractories	20	1520	2766	1530	2786
Refractories	23			1580	2876
Refractories	26			1595	2903
Clay Testing (PCE)*	27			1605	2921
Clay Testing (PCE)*	28			1615	2939
Clay Testing (PCE)*	29			1640	2984
Clay Testing (PCE)*	30			1650	3002
Clay Testing (PCE)*	31			1680	3056
Clay Testing (PCE)*	32			1700	3092
Clay Testing (PCE)*	33			1745	3173
	34			1760	3200
	35			1785	3245
	36			1810	3290
	37			1820	3308
	38			1835	3335
	39			1865	3389
	40			1885	3425
	41			1970	3578
	42			2015	3659

* Pyrometric Cone Equivalent.

"Cast iron sanitary ware is usually produced by the dry process, most other ware by the wet process.

"Formerly all enamel plants produced their own frit. More recently large supply houses have marketed increasing amounts of frit to the smaller, and many of the larger enameling concerns. The frit as purchased by the enameling plant is ready for milling. Most of the frit thus purchased is for wet process enameling, in accordance with the above method.

"There is an increasing demand for enameled commodities as the merits of vitreous enamel become better recognized in a great variety of uses. Formerly the chief outlet was in the form of sanitary and cooking ware. Then came vitreous-enameled signs, stoves, refrigerators and dairy, canning and chemical equipment. The present rapid expansion involves a multitude of uses including parts for buildings. The future possibilities are almost unlimited.

"The following may be taken as a typical white enamel for sheet iron:

White Frit	Per cent	Mill charge
Feldspar	29.5	
Borax	22.0	100 lbs. Frit
Silica	19.0	6% Clay
Cryolite	13.5	5% Tin oxide
Soda ash	3.5	
Fluorspar	3.5	
Sodium nitrate	3.0	
Antimony oxide	3.0	
Zinc oxide	3.0	

"As to colors, certain general facts may be stated: Red colors are usually made from iron, cadmium and selenium compounds. Greens are made from chromates or chromates properly combined with other mineral oxides. Yellow is produced from compounds of antimony, uranium and titanium. Blues are usually based on cobalt compounds, in combination with other mineral oxides to vary the color.

"There are three general ways of producing the desired colors. For the darker blues and black, coloring oxides are usually smelted in the frit. For certain other colors a relatively clear frit or glaze is used, the color and opacity being produced by mill additions. For the more delicate an opaque frit, such as given in the formula above, is used, and coloring oxides and varying amounts of opacifier are added at the mill."

OTHER PATENTS

U. S. Patent 1,844,670, manufacture of an improved vitreous, acid-resisting enamel; 1,785,777, preparation of a slip for vitreous enamels consisting of an acid-resisting glass, titanium sulfate, and English pipe clay; 2,048,319, producing cast refractories; 2,069,059, method of producing ceramic ware.

PROBLEMS

1. A kiln packed with saggers contains in all 2200 dozen pieces of tableware. Each piece weighs ½ pound, and there are required 3 pounds of coal for each pound of ware fired. How many tons of coal are needed in all? With coal at $4.00 a ton, what is the fuel charge against each dozen pieces?

2. A ware is made from a clay mixture which contains exclusively china clay, flint and feldspar. The feldspar in the batch is 22.5 per cent on the dry basis. The final ware contains 68 per cent SiO_2. Taking the formula in the text as the composition of the feldspar, the composition of the china clay in the text as applying, and the flint as 100 per cent SiO_2, how much of each raw material would you have to take, for each 100 pounds of ware?

3. It is required to smelt $2\frac{1}{2}$ tons of frit for a white vitrified enamel of the formula given in the text. Assume a loss from all sources of 5 per cent. How many pounds of each of the materials listed will be required, if the loss is spread over all the items uniformly? It must be remembered that sodium nitrate and soda ash lose gases during the smelting as a normal reaction; in finding the theoretical yield, which must be done first, sodium nitrate and soda ash should be changed to their sodium oxide equivalent.

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"The manufacture of ceramic decalcomania," G. H. Stapleford, *Bull. Am. Ceramic Soc.*, **15**, 335 (1936).

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It is essential that window glass should be an inexpensive commodity in order to permit its use in the most modest of dwellings. Ingenious improvements in its manufacture have made it possible to keep it low-priced in spite of the general increase in cost of labor and materials. Window glass which will not filter out the vital short rays of light is being placed on the market, a tremendous contribution toward the general health of the people.

Chapter 11[1]

Structural Glass, Optical Glass, Special Glass, Glass Bottles

Structural glass includes window glass, wire glass, figured rolled glass, plate glass, and health glass; of these, ordinary window glass ranks first in the amount produced.

Window glass in the United States is made exclusively by mechanically drawing a flat sheet of glass, which passes through a lehr on its way to the cutter and requires no subsequent annealing nor flattening of any kind. There are three processes which are in use, and which differ as follows: In the Fourcault process, the sheet forms in the slot of a clay block pressed into the glass melt by adjustable arms; it may very properly be said to be extruded. After being formed, the sheet is carried vertically upward through the lehr, reaching finally the cutting platform above it. The original patent rights have run out.

In the Colburn process, the sheet is formed with the help of two edge guides in the glass melt; it rises vertically at first, then turns a right angle over rolls and travels horizontally through the lehr.

Finally, in the Pittsburgh Plate Glass Company's process, the sheet is formed without clay block, and rises vertically through the lehr, as in the Fourcault process.

The molten glass for all three processes is obtained by heating together soda ash, lime, sodium sulfate, charcoal or other forms of carbon, sand, and cullet (broken glass), in a large trough-shaped furnace. Window glass is a soda-lime glass.

THE FOURCAULT PROCESS

Perhaps a fourth of the window glass made in the United States is made by the Fourcault process, modified more or less by each operating company's experience. The furnace has several small extensions called the work pits, in each of which one drawing machine operates. In order to have a definite furnace for study, the furnace of the Adamston Flat Glass Company at Clarksburg, W. Va., will be described, and all modifi-

[1] Reviewed by Mr. Donald E. Sharp, Consulting Engineer, of Bailey and Sharp Co., Glass Technologists, Hartford, Conn.

cations given of the original Fourcault procedure will be those developed at the Adamston plant, one of the most successful of the many Fourcault units.[2]

The Furnace. The furnace is of the continuous type, with continuous feed, fired by gas, either natural gas, which is not preheated, or by producer gas, which is preheated. The combustion air is preheated in either case, by passing it through the regenerators located below the furnace.

The plan of the furnace with the exact dimensions is shown in Figure 55. It is built of three kinds of bricks and forms: (1) Silica bricks for the
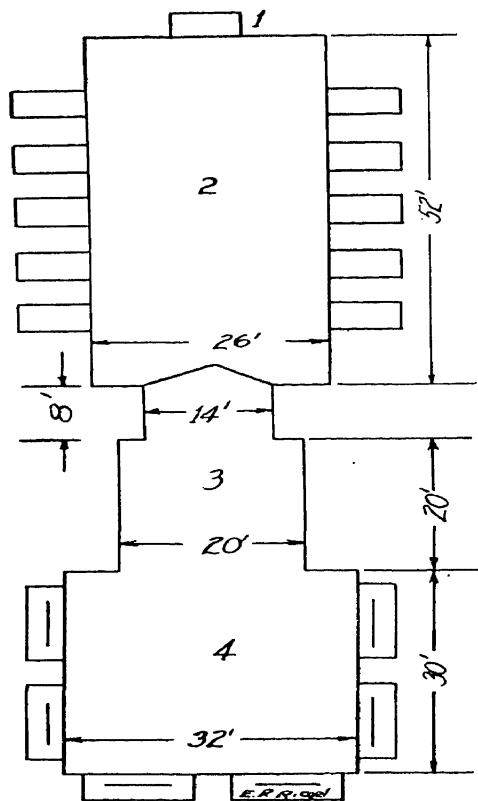
FIGURE 55.—Plan of furnace for window glass by the Fourcault machines. 1, the dog house, or charging trough; 2, melting end; 3, refining end, with neck between 2 and 3; 4, drawing chamber, surrounded by the work pits, each one with its drawing machine. Between the melting end and the neck are the floaters. The five inlets on each side of melting end for combustion air and gas are shown.

roof, or arch, commonly called the "cap"; (2) "Refractory" blocks for those upright walls which do not come in contact with the molten glass; and (3) "Flux" blocks, a special composition of fire-clays which resists glass attack, and which is employed for those walls which come in contact with the molten glass. A fourth kind of brick and shaped slab has been introduced in the construction of glass furnaces, namely, the Corhart[3]

blocks; they have a very dense structure and are extremely resistant to the corrosive action of molten glass.

After its construction, the furnace is heated gradually, when it undergoes expansion. In order to accommodate this expansion, the roofing arch rests on skew-backs which are carried by horizontal steel beams integral with steel uprights. The distance between the latter is adjustable by working the nuts on the tie rods which extend the width of the furnace and connect the steel uprights. The loosening of the nuts is done gradually, as the heating progresses.

Once in operation, the furnace never stops; it runs day and night until it has deteriorated so much that it must be rebuilt.

There are five regenerator sets on each side of the melting end of the furnace, each one double, one chamber for air, the other for producer gas. (*See* Figure 56.) The regenerators consist of brick chambers filled

FIGURE 56.—The regenerative chambers for air and gas. As shown in sketch, the chambers at the right are giving up their heat; those on the left are storing heat. The chambers are filled with a checker work of bricks.
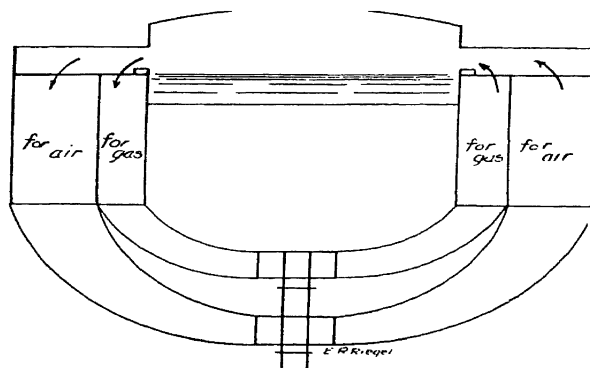
with a checker-work of bricks; they are situated on a lower floor, with the inlets to the furnace built onto the side-walls of the furnace proper. When natural gas is used, it is not preheated, but enters directly from the conduit through a flare in the wall of the air inlet, close to the burning space.

When producer gas is used, the gas leaves the producer hot and is prevented from cooling by insulation; it reaches the regenerator bricks (south side for instance) at 1100° to 1300° F. (600° to 704° C.); the regenerator raises it to 1800° F. (982° C.). The air in the meantime is brought to 2200° F. (1204° C.). Gas and air meet just inside of the furnace, so that the flame forms inward, and sweeps cross the width of the furnace, passing out through the regenerators on the other side (north side), which now are brought to a high temperature. After 20 minutes, the direction of the gas and air is reversed; they enter through the regenerators at the north side, sweep across the furnace and now heat the regenerators on the south side. The reversing is done by hand.

There takes place a gradual eating away of the brick at or below the level of the glass, especially near the "dog house." The present remedy is to install a set of water-cooled pipes in contact with the outside of the

blocks at the regions of greatest corrosion. These reduce the degree of corrosion, but even with these aids, blocks sometimes are completely eaten away, until the glass itself is in contact with the water coolers. The glass congeals and forms its own retaining wall at those places. Thanks to this innovation, the life of a furnace has been greatly extended. One run of 39 months is on record; a life of 24 months is considered satisfactory, while formerly, 9 months was a long life.

Materials. The materials for making glass are fed in at the "dog house." A batch of 1175 pounds of the mixed raw materials, and 1175 pounds of cullet are introduced every half hour. The batch consists of

	Parts
Sand	100
Soda ash	30
Lime CaO	16
Salt cake	12
White arsenic	0.5
Powdered cannel coal	0.5

The materials are fed from overhead bins into a mixer suspended on scales, carefully weighed and thoroughly mixed. The cullet (broken glass) comes partly from the plant and partly from outside purchase.

As the materials enter the furnace, they gradually melt, but evolve gases quietly. Looking into the furnace, the surface is white for a distance of six feet; small pits about 1 inch across may be seen; these are the "rabbit tracks." Further out, there still is much white matter, and a pattern not unlike ribbed sea-sand is visible; these are "gingerbread". A small pool some 6 or 8 inches across, caused by excess salt cake, and which the glass man dreads, is called "salt water." One-third of the way down the melting end, glass has formed, and no whiteness is visible any more.
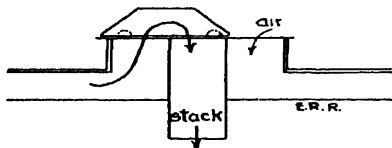
FIGURE 57.—The device for reversing the direction of the flame. A box with open bottom is set as shown, when chambers at the left in Figure 55 are storing heat. After 20 minutes, it is moved to the right, and the inlet for air is then the left passage.

Just in front of the floater, the operator watches for a faint line of white bubbles, which should be absent.

The reactions in the furnace probably are:

$$Na_2CO_3 + k . SiO_2 = Na_2O . k . SiO_2 + CO_2$$
$$CaCO_3 + m . SiO_2 = CaO . m . SiO_2 + CO_2$$
$$Na_2SO_4 + \tfrac{1}{2}C + n . SiO_2 = Na_2O . n . SiO_2 + \tfrac{1}{2}CO_2 + SO_2$$
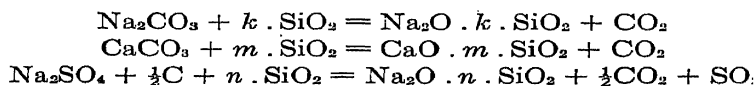
with $k + m$ a little over 5 in this case.

Between reversals of gas and air (*see* Fig. 57), the furnace is absolutely quiet for some thirty seconds, and a view may be had of the

glass pool which reflects every detail of the roof and sides; so quiet is the pool that it takes a little study to tell where glass ends and exposed wall begins. It is a beautiful sight; a moment more, and the flames have appeared and fill the whole space, cutting off the view.

The hottest part of the furnace is half way down the melting end, 2600° F. (1427° C.); at the floater hole, just in front of the floater, the glass itself is 2430° F. (1332° C.).
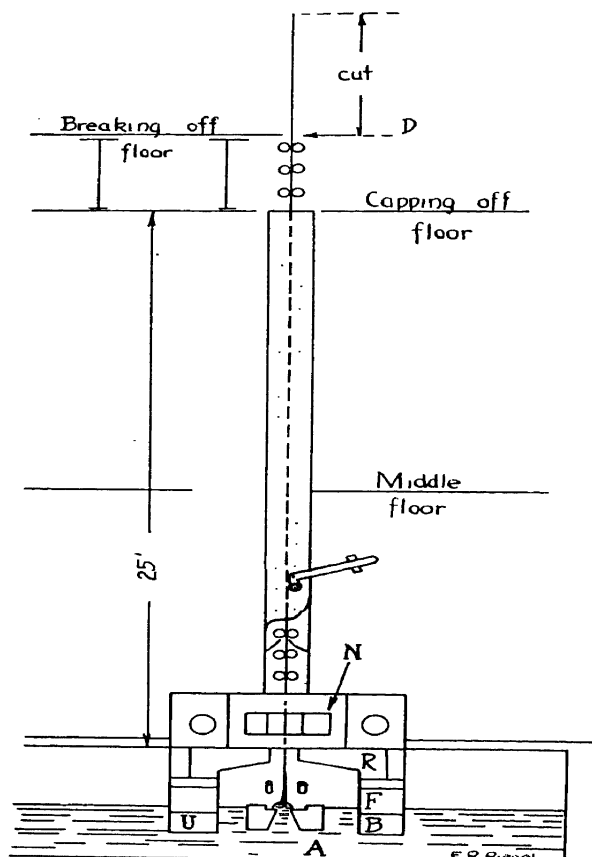
FIGURE 58.—Side elevation of a Fourcault drawing machine. *A*, the débiteuse, clay block with slit; *U* and *B*, under-bridge; *F*, bridge; *N*, annealing box with burners; *D*, level at which diamond line is drawn. The sheet coolers are shown just above the débiteuse.

The gas consumed per day is 800,000 cubic feet for natural gas. The capacity of the furnace is 1200 tons of molten glass, when the level is carried at 58 inches. One inch in height represents 22 tons of glass. The work pits draw 50 tons of glass a day.

There is a normal shrinkage in the weight of the charge, due to the loss of gases; it is increased further by the volatilization of some alkali oxides. The observed shrinkage is generally 10 per cent (see problem 3). In other words, for 100 pounds of raw materials charged, 90 pounds of glass are drawn from the furnace.

Work Pits. The glass travels through the neck into the refining end, finally reaching the work pits where the drawing machines are situated. The temperature of the glass in the pits is 1860° F. (1016° C.).

The essential feature of the Fourcault process is a long rectangular clay piece, with a longitudinal slot, through which the melted glass is "paid out", hence the term, the débiteuse. The shape of the débiteuse is shown in the adjoined elevation of the drawing machine. The clay block floats on the glass, and is forced down a short distance into the glass melt by adjustable arms; its delivery slot is protected by raised edges, so that no glass reaches it from the surface, but a gob is forced up from below. It is this body of glass which is pulled up by the preceding parts of the sheet, to become itself a flat sheet. The action will be clear from Figure 58. The sheet enters the lehr, and is pulled up by the asbestos rollers which bear against it. The rollers on the left side are driven; those on the right are suspended on hinges and free to move outwardly; they bear against the sheet by the weight placed on the outside arm of the hinge.

A flame plays in the heating box and its heat warms the lehr, the temperature gradually decreasing as the distance from the annealing box increases. It reaches the end of the lehr, emerging onto the cutting platform, where it is cut into sheets. A straight line is made by a steel wheel cutter by pulling it across while resting on a light wooden frame which the rising sheet lifts with itself. The lehr is 25 feet high, and the time of annealing varies with the speed of drawing, from 11 minutes for the lightest glass to 45 minutes for the heaviest.

A vane under each of the rollers deflects any broken glass which may drop down the lehr, and ejects it through small swing doors.

The Thickness of the Glass. The same débiteuse serves for all thickness (called "strengths" in the glass factory) of glass; the strength is controlled by four factors: (1) Temperature, the higher it is, the thinner the sheet; (2) depth of block in the melt, the deeper it is, the thicker will the sheet be; (3) sheet coolers, the closer, the thinner the sheet; (4) the speed of draw, the higher the speed, the lower the "strength." The rates of draw are roughly as follows:

	Inches per minute	Width, inches	Annealing time, minutes
For single strength	28	62	12
double strength	18	63	17
heavy strength ($\frac{7}{6}$ inch)	11	65	27
heavy strength ($\frac{1}{4}$ inch)	7	65	45

As the sheet forms, a heavy edge develops and necessitates a recess in the asbestos drawing rolls, as indicated in Figure 59. The edges of the sheet are removed on the cutting floor, by trimming 3 or 4 inches off the sides, and are sold for glass shelvings in small medicine closets, show counters and the like. The cut sheets are placed in a warm dilute hydrochloric acid bath for a short time, to remove sublimed alkali which later would cause dullness.

From the cutting floor, the cut sheets are wheeled to the cutting room, where the glass is sorted and defects removed, always with the precaution to produce useful sizes. The grades are A, B, and C, defined by one of the government agencies.

The largest sheet made by this process is 120 inches by 60 inches.

FIGURE 59.—Horizontal cross section through the Fourcault lehr, showing two asbestos rollers, and the glass sheet with its thickened ends. The rollers are made smaller in diameter at the ends in order to accommodate this extra thick-
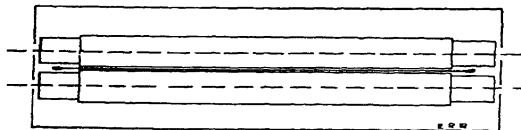
General Remarks. A slight change in temperature may throw a furnace out of its stride, and it may be two weeks before it is brought back to correct production. A change in temperature may cause "stones" in the sheet, which make it unsalable. In addition, there may be blisters, seeds, and waves, due to various derangements. The heat on a glass furnace is not watched in order that it may show a nice balance, but the wise operator spends plenty of money for heat in order to insure steady production of the higher grades; it takes very little time to lose the equivalent of a fuel bill in poor glass. The choice of the composition of the glass is of the greatest importance; in order to indicate the general trend, it may be said that the short period of annealing calls for a softer glass, richer in alkali than would otherwise be necessary.

THE COLBURN PROCESS

The process depends upon the special machine invented by Colburn [4] and gradually perfected. This machine consists of a cylindrical roller over which the sheet of plastic glass is bent from its original vertical position to the horizontal position; of a bar which starts the sheet; of small knurled cold rolls which set its edges; of grip bars placed beyond the bending roll which pull the sheet along; of a flattening table, and a lehr. In addition numerous auxiliary devices, each one indispensable, and perfected through trial, are part of the process. Nearly all the essential features are covered by patents.[5] (*See* Fig. 60.)

The following description of the process is taken from a booklet published by the company using the furnace:

"To start the drawing of the sheet the Colburn machine is placed in reverse motion, which allows a bait to be introduced into the drawing pot containing the molten glass. The bait consists of a flat iron bar 3 inches wide and about 6 feet long, attached to the strips of flexible

[4] Irving W. Colburn, whose process, with certain improvements, is now used by the Libbey Owens-Ford Glass Co., Toledo, Ohio. The plants are located at Toledo, O., Shreveport, La., Charleston, W. Va., Rossford, O., Ottawa, Ill.

[5] The bending roll, in U. S. Patent 836,439, Claim 21; the bearing belt and grip bars, U. S. Patent 849,351 and 876,267; the knurled rolls in U. S. Patent 970,182, Claim 2

metal which allow the bait to pass over the bending roll, down into the glass. The molten glass immediately adheres to this bar. Then the machine is placed in forward motion thus pulling the bait with its adhering mass of plastic glass over the bending roll into the flattening table and thence into the lehr. When the bait reaches the end of the flattening table, about ten feet from the bending roll, it is cracked off and removed; and the sheet of glass continues on its way, through the 200-foot annealing lehr.
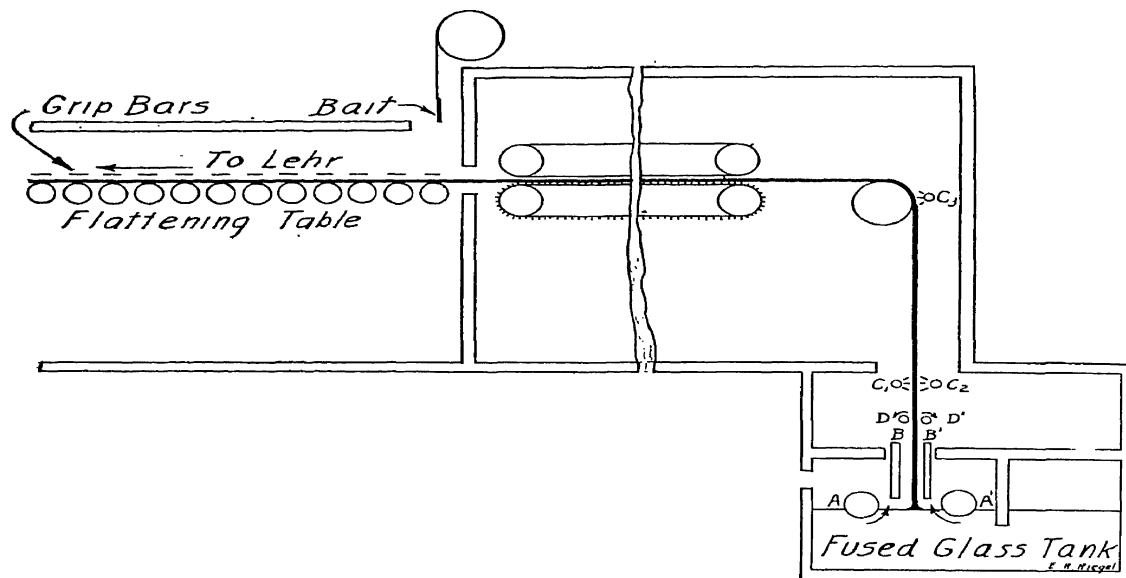
FIGURE 60.—Side elevation of scheme for making window glass by the "flat glass" system. *A*, *A'*, rollers of the same width as the sheet which feed the glass to the point of draw; *B*, *B'*, water-cooled shields which protect the sheet from flames from near-by burners; C_1, C_2, C_3, flames to keep glass from cooling below the plastic stage; *D*, *D'*, are water-cooled knurled rolls which form the edge of the sheet and pull on it; there is a pair of such rolls on each edge of the sheet. The edges are formed thicker than the main part of the sheet.

"During the drawing the sheet is kept at an even width by passing the outer edges of the sheet between two sets of water-cooled knurled rolls placed an inch or two above the surface of the molten glass, just inside the edges of the drawing pot. These knurled rolls engage the sheet for about two inches on each side and serve to sustain it at a constant predetermined width. These edges are thicker than the intervening sheet of glass, and the real pulling of the sheet is accomplished by engaging the outer edges of the sheet—after it has passed over the bending roll—between the flattening table and a series of grip bars running in the same direction and placed just above the flattening table.

"The lehr is provided with two hundred power-driven rolls, covered

with asbestos composition, over which the glass passes in continuous sheet form, emerging at the end onto a movable cutting table. Here it is cut into sheets of suitable size, dipped in a hot solution of hydrochloric acid and then distributed to the cutting stalls. The sheets are graded and cut into commercial sizes and packed in boxes each containing fifty square feet of glass. This sheet glass is absolutely flat and free from the distortions ordinarily noticed in window glass." [6]

The batch for this process is made up in approximately the following proportions: 100 parts sand, 35 of limestone ($CaCO_3$), 28 of soda ash, $6\frac{1}{2}$ salt cake and 0.6 of carbon.

The Pittsburgh Plate Glass Process

In this method of working, the sheet is drawn from the glass melt directly, as in the Colburn process, and raised vertically through the lehr, as in the Fourcault process. The task in any of these processes is to prevent the glass sheet to pull itself, while still soft, into a V-shape. What the débiteuse does in the Fourcault, and the knurled rolls in the Colburn, is done in Pittsburgh Plate process by four drawbars reaching under the glass, with balls at their ends. The bars and balls rotate, in the sense which pulls the glass sheet outward, counteracting its tendency to lose width. As soon as the sheet is lifted out of the melt, the glass has enough set so that the danger is past.

This process avoids the lines which irregularities in the débiteuse are supposed to cause on the surface of the Fourcault sheet, and also the irregular stresses attendant to the bending of the sheet through a right angle, as is done in the Colburn system.

Hand-blown Window Glass, and the Machine Cylinder Method. The old way of making window glass was to blow (from the lungs) at the end of an iron blow-tube or pipe, held in the hand, cylinders not over 5 feet long nor over 15 inches in diameter. The glass had to be reheated before the glory hole several times, reblown, then the two ends removed. The cylinder so obtained was cut lengthwise, and allowed to flatten in a furnace similar to the one used in connection with the machine cylinders.

In the machine cylinder method, cylinders 48 feet high and 28 inches across were drawn upward by mechanical means. The cylinder was cut into 5-foot lengths, then halved, and the halves flattened in an auxiliary furnace with a turn table. The process became obsolete, at least in the United States, when patent protection on the Fourcault process came to an end.

Wire Glass. Wire glass is an important structural glass. It is made by laying a steel wire netting into soft glass between two rolls immediately after the glass has been fed from the furnace. The operation may be a continuous one, and a sheet 5 feet wide may be made at the rate

[6] "Flat Glass" by Arthur E. Fowle, The Libbey-Owens Sheet Glass Co., Toledo, Ohio, published by the company in 1924.

of 20 feet a minute; it is cut by bending it in the shape ⌐L, when the wire breaks off easily. (*See* Fig. 61.)

Figured glass, often called Florentine glass, is made by forming the sheet between two rolls, which may have a design cut on one or both. When the design is a square or a cube which must retain the proper shape to give the desired effect, the sheet may be formed on a table, and a roll bearing the design passed over it.

Plate Glass. The composition of plate glass is approximately the same as that of window glass; it is a lime-soda silicate, but is thicker than window glass, for the sake of strength in the finished plate, and also to prevent, or better, reduce breakage in the long process of grinding and polishing which it invariably undergoes. In fact the distinguishing feature of plate glass is that it is free of distortions, that its surfaces are absolutely true. Attempts to produce a sheet of glass thick enough
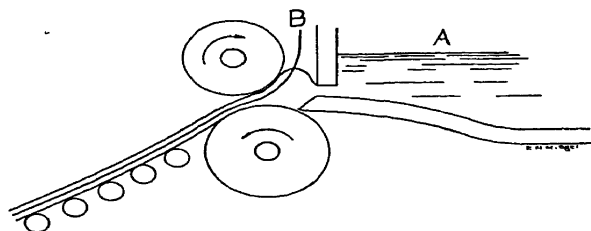
FIGURE 61.—Apparatus for the continuous drawing of wire glass. *A,* the glass furnace, working end; *B,* sheet of iron wire.

to have the strength desired in large sections without grinding and polishing have been successful; by means of the P. P. G. or Colburn process, such plate can be made and is made.

Plate glass by the standard, older process is poured in single sheets. The furnace may be of the continuous type, as for window glass, or pots may be used; the latter case is the more common. The glass from a pot, lifted by mechanical tongs, is poured onto a cast iron table (built of segments) and leveled by a heated roller. The rough plate is annealed, then set in plaster paris on a flat table, ground with 5 grades of sand, decreasing in coarseness, then 5 grades of emery,[7] and polished with rouge.[7] Both sides of the plate receive this treatment, in the course of which about half the thickness of the glass is lost.

Continuous Sheet Process. In this process[8] the glass flows from the furnace onto the metal table, and is leveled by passing under two nichrome cylinders, the second smaller than the first. The glass sheet continues into the lehr, 500 feet long, where it cools from about 1100° F. (593° C.) at the entry to 100° F. (38° C.) at the exit. It is cut into suitable sizes, mounted in plaster paris, and ground and polished as single

[7] Emery is the natural crystallized alumina (Al_2O_3); rouge is the oxide of iron obtained by roasting copperas ($FeSO_4 . 7H_2O$).

[8] "Making glass for Ford windshields," F. J. Huntley, *The Glass Industry* (1923), **4,** *p.* 1; "Continuous process for plate glass at Ford River Rouge plant," E. P. Partridge, *Ind. Eng. Chem.,* **21,** 1168 (1929).

plates. This process is well adapted only for fairly small pieces of uniform size, such as windshields for Ford automobiles.

The most recent process for high quality plate glass is that of Bicheroux,[9] in which the melted glass is poured between two rollers; the sheet comes out on a moving table, is fed to a lehr, annealed, and cut into suitable lengths. The grinding and polishing are the same as described above.

Health Glasses. In order to permit the short invisible rays of the sun to reach the inside of dwellings and offices, the glass for the window must be selected for its transparency to such rays. Ordinary window glass stops them by absorption. A window pane of clear quartz glass is transparent to solar ultra-violet rays, but quartz glass is too expensive for general use. Corex, made in several grades, may be a phosphate glass, or it may have a composition similar to that of pyrex. The phosphate glass has a transmission practically equal to that of quartz glass, but is not completely resistant to atmospheric moisture. The borosilicate corex transmits much of the solar ultra-violet, and is very resistant to atmospheric attack. Vitaglass is one of the most promising of the health glasses developed recently; it has a good ultra-violet transmission, and is relatively inexpensive.[10] It is a soda-lime glass of special composition and refinement. Substances other than glass are transparent to the solar (and still shorter) ultra-violet rays, such as Aldur,[11] a urea-formaldehyde condensation product, colorless and transparent in the visible.

The health glasses undergo solarization, that is, when first exposed to the sun, the original transparency to the short rays diminishes by 20 per cent; after this loss, the glass is stabilized, and continues to transmit a constant percentage of solar ultra-violet rays.

The percentage transmission of a number of materials, the range in which they transmit, and also, the range of solar short rays, are indicated in Figure 62.[11]

Safety Glass. Safety glass consists of two sheets of plate glass cemented together by a sheet of pyroxylin or thin Celluloid, forming as transparent a whole as the component parts singly. Such laminated glass may be shot through by a bullet, without falling to pieces; it breaks, and is pierced, but the segments remain in place. Safety glass is used for automobile windshields and windows, and has been a major factor in reducing injuries and deaths in collisions.

In the earlier forms, the Celluloid sheet often turned yellow and brown-red. This was due to the action of ultra-violet light which was able to penetrate the glass; the difficulty is met by adding iron to the

[9] Described in "Die Glassfabrikation," Dralle-Keppler, Oldenburg, Verlag Fischer, Vol. 1, 1926; Vol. 2, 1931, which gives the list of patents on this process.

[10] Buildings glazed throughout with Vitaglass include, in New York: Medical Arts, Equitable Trust Co., International Telephone & Telegraph Co., San Carlos Apartments, Anthony Campagna Apartments.

[11] "Ultra-violet transmission of a new window-glass substitute," R. H. Crist, *Ind. Eng. Chem.*, 20, 1367 (1928), and: "Special characteristics of light sources and window materials used in therapy," W. W. Coblentz, *Trans. Illum. Eng. Soc.* (*N. Y.*), 23, 247 (1928).

glass batch (whereas usually it is carefully avoided) so that the glass shall be non-transparent to the ultra-violet light.

There are two methods of assembling. In the dry method, the glass is coated with an aqueous glue solution containing a preservative, dried, and the pyroxylin sheet placed between two glass plates, sandwich fashion. The assembly is placed in bags, evacuated, then taken out and sealed along the edges. In the wet method, the glass receives a resinous lacquer coating; the pyroxylin sheet receives on both sides an intermediatory bonding solution; the pieces are assembled, and after evacuating, sealed all around.
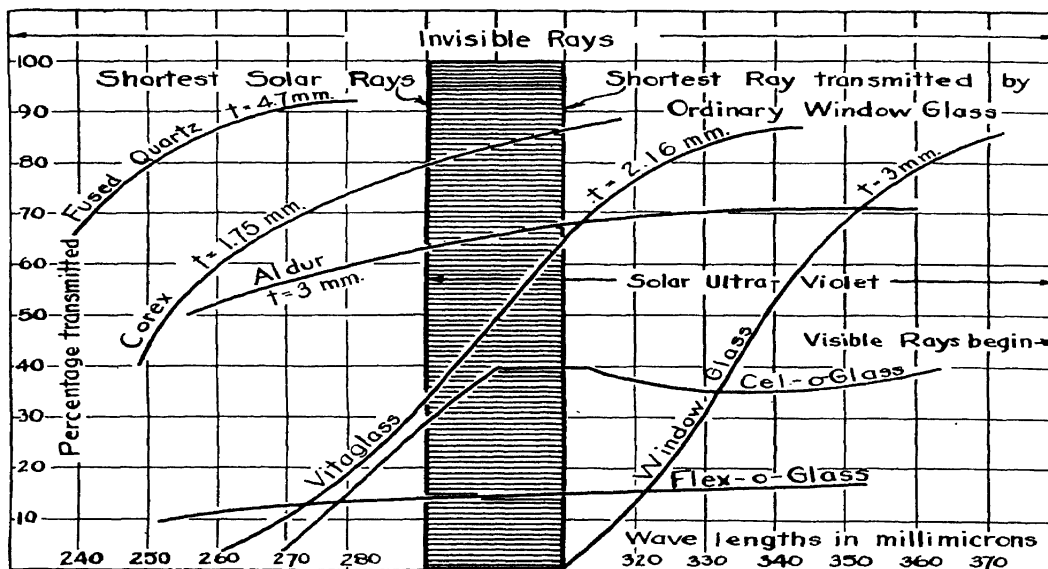
FIGURE 62.—Curves showing the percentage of short light rays transmitted by various glasses and other substances. The thickness is given as "t." The shaded area represents the "vital rays." (*See references in text.*)

At temperatures below 0° F. [− 18° C.] safety glass of the standard type is no longer safe, while at temperatures above 120° F. [49° C.], there is danger of softening of the pyroxylin film, and again the glass has no longer the quality of "safety." The use of vinylite resins has been proposed as a remedy, and a combination of several plastic sheets, such as the pyroxylin sheet with one of methacrylic ester resin.[11a]

An entirely different safety glass is quenched glass, a single sheet, but with hard surfaces produced by quenching, and a softer, more elastic interior layer. Such a glass is expected on the market at any time now.

Mirrors. The plate glass is cut to size; it is examined for even the slightest blemish, such as a scratch, which would cause an ugly spot in

[11a] U. S. Patent 2,032,663. This patent gives the safety range of regular. Celluloid-laminated glass as 120° F. to 60° F.

the finished mirror; all blemishes are removed by polishing with rouge. As a rule the sheet is first beveled, freed from blemishes next, and is then ready for the final step, the coating with silver.

Just before silvering, the glass is scrubbed, rinsed with distilled water, and flushed with a reducing solution, such as stannous chloride or an organic reducer. Without draining it, the sheet is quickly placed on a cast-iron hollow table top covered with felt, and kept warm by steam in the internal chamber. The glass is leveled by means of wedges and a soft pad under the center, to prevent sagging. A solution of silver nitrate, slightly ammoniacal, is poured on from a pitcher and the sheet left undisturbed for an hour. A lustrous deposit of silver gradually forms. Next the deposit is dried, coated with shellac, and later with paint.

Other procedures include, after thorough cleaning, a preliminary treatment with 0.1 per cent stannous chloride solution for $\frac{1}{2}$ minute, rinsing, and application of the mixed silver solution, containing the reducing agent added just before use. This latter agent may be formaldehyde, glucose, Rochelle salt (requires boiling), tartaric acid, and others.

A formula might be: *A*, silver nitrate 10 grams, distilled water 90, ammonia to precipitate and then redissolve the precipitate, enough more water to make 1000 cc.; filter. *B*, silver nitrate 2 grams, dissolve in 10 cc. water, dilute by adding boiling water to make 1000 cc., then add 1.66 grams Rochelle salt and continue boiling for 20 minutes, until nearly clear; filter hot, and cool to room temperature. Equal parts of *A* and *B* are mixed just before using.

The solutions need not be hot, they may be used cold, when a harder film is produced. More dilute solutions produce a thinner film, which may even be transparent.[12]

Double-walled Dewar flasks are generally silvered, and known under the trade name of "thermos."

SPECIAL GLASS

Special glasses are those which serve special purposes, and must possess those properties which make them suitable. The special glasses are optical glass, thermal glass, chemical glassware, cut glass, and colored glass. Compared with window glass, the tonnage they represent is insignificant; on the other hand, their price is high.

The materials for the manufacture of *optical glass* must be purer than for common glass, and the variety is greater. Two properties of glass are chiefly the concern of the optical glass maker; they are refraction and dispersion.[13]

The term crown glass means a glass of low refraction and low dispersion; flint glass means a glass of high refraction and high dispersion.

[12] "On the silvering of glass," by Donald E. Sharp, *Glass Ind.*, **11**, 273 (1930).
[13] By "mean dispersion" is meant the difference between the index of refraction for the red line of hydrogen n_C and the index for the blue line n_F. This difference is not the same for various glasses. The dispersion for any two lines may be studied.
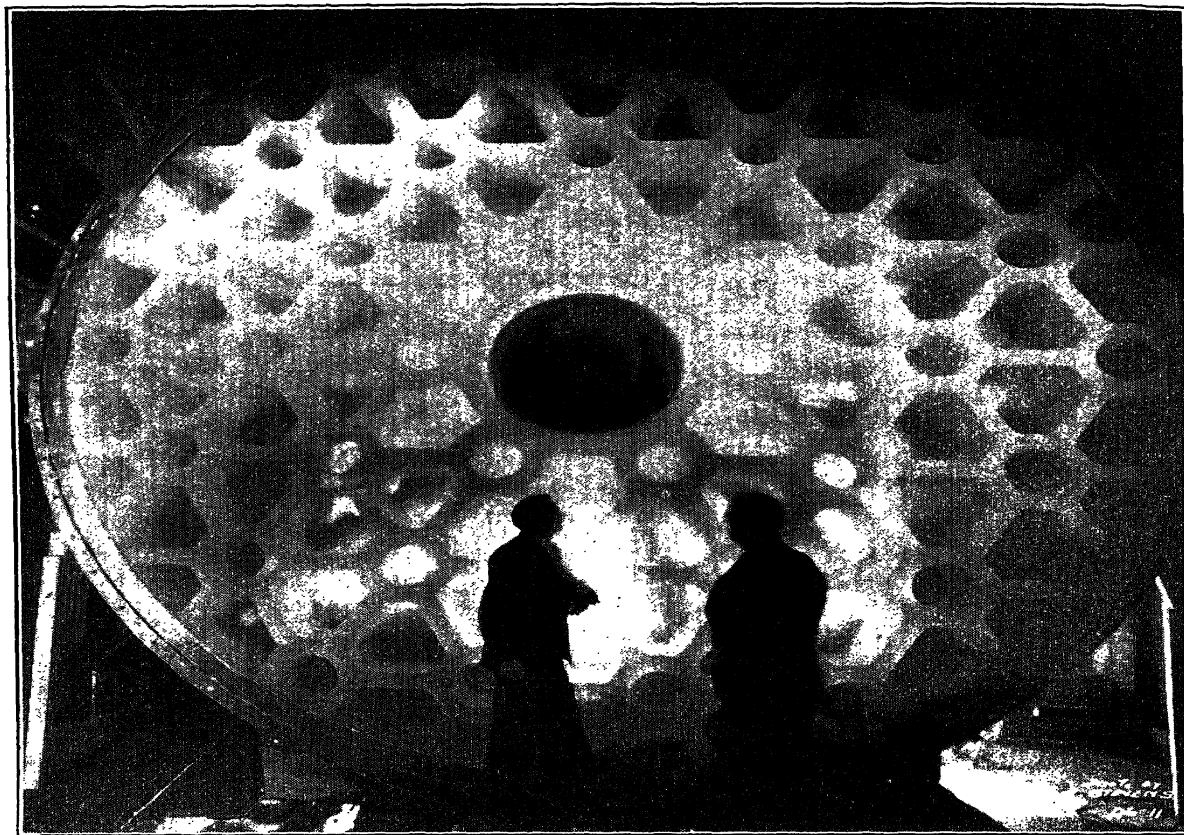
FIGURE 63.—The Pyrex Glass telescope disk, 200 inches in diameter, after the core material had been removed and the surface cleaned by sandblasting, seen from the under side. The figures are Dr. G. V. McCauley (left) and Dr. J. C. Hofsteder, in charge of the work. (By special permission from the Corning Glass Company.)

This rough classification serves well for general purposes. It might be added that crown glass is a lime-soda glass, hence essentially the same composition as window glass; flint glass is a lead-potassium glass. A more accurate division is the following: In the expression

$$\nu = \frac{\text{refractive index} - 1}{\text{dispersion}}$$

the glasses of the crown glass type have a ν value generally over 55; those of the flint glass type have a value below 55.

Optical glass is made in small batches, which are melted in individual pots.[14]

Much attention was devoted by the general public to the casting and transporting of a *200 inch diameter Pyrex Glass reflecting telescope disk,*

[14] Optical glass was treated somewhat more fully in the second edition.

cast in Corning, N. Y., and shipped to Mount Palomar, California. It is the largest disk to be cast, is 26 inches thick, and weighs 20 tons; special apparatus had to be constructed. The reflecting surface of the disk is polished, and coated with aluminum. As shown in the picture, there is a ribbing reinforcing the disk proper; the purpose is to stiffen it, for without it, its own weight, when tilted, would cause enough flexing to make some of the measurements valueless.

Thermal Glass and Chemical Glassware

Window glass is used because it admits light into buildings, and because it is cheap. Optical glass is used in order to refract light, disperse, or condense it. Thermal glass owes its economic existence to its low coefficient of expansion: it can be heated rapidly, or cooled suddenly and unevenly without breaking. The best known of such glasses is Pyrex Glass, which is made into baking dishes, teapots, and laboratory glassware. The breakage of Pyrex Glass beakers and flasks is so low and its resistance to chemical reagents so high that it has been universally endorsed in nearly all laboratories, in spite of its somewhat higher price than common glassware. Before the war Jena glass, also a remarkable heat- and shock-resisting glass, was largely used in the United States.

The composition of these two glasses follows:

	SiO_2	B_2O_3	Na_2O	Al_2O_3	As_2O_3	K_2O	MgO	CaO	Fe_2O_3	ZnO
					Per cent					
Pyrex	80.62	11.90	3.83	2.00	0.66	0.61	0.29	0.22	0.12	....
Jena	64.58	10.03	7.38	6.28	...	...	0.12	0.08	0.10	11.78

Cut Glass. Lead glass is used in the manufacture of cut glass because of its brilliancy. Batches vary, but a fairly representative one for the melting of such a glass might be the following:

Sand	1000	parts
Red lead Pb_3O_4	660	"
Pearl ash K_2CO_3	380	"
Salpetre KNO_3	130	"
White arsenic As_2O_3	10	"

The article is shaped by pressing or blowing, cooled in the annealing furnace, and passes thence to the cutting room. The design is drawn on the glass with a grease pencil, and is then cut in by means of a small metal or alundum wheel and emery; the surface of the cut is next polished with rouge applied on a wooden wheel. True cut glass may be distinguished by its sharp edges; imitation pressed ware lacks these. For cheaper varieties, the design is pressed in and just enough cutting and polishing done to give the characteristic edges. The cutting of glass is also combined with etching to good advantage.

In table glassware, ordinarily called *decorated glassware,* a design may be cut on the alumina or other wheel consisting of a series of small circular or oval areas. These are then dull in appearance, similar to

poorly frosted glass. The original brilliant surface may be restored by submerging the glasses alternately in a bath of sulfuric acid, containing some hydrofluoric acid, and in warm water.

COLORED GLASS

The expansion of automobile manufacture and the construction of subways, added to increased demands for railway and maritime signals, has raised the importance of the colored glass production. To these utilitarian purposes must be added the uses of colored glass in tableware, and in the art of constructing colored windows.

The practice in making red automobile tail lights will serve as example of manufacture for the smaller pieces. A batch of the red glass is prepared in closed pots (Figure 64); the composition may be, for in-
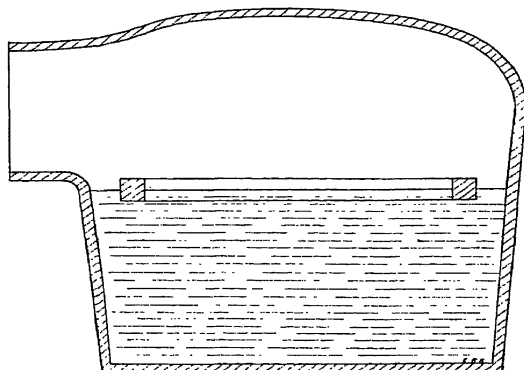
FIGURE 64.—Closed pot used for small lots of glass of window-glass grade and for colored glass.

stance, soda-zinc, with 1 per cent selenium. The pot is served by two men and one boy; one takes gobs of clear glass from the inner ring in the pot, and places them in a mold, disconnecting the gob by means of shears from the pipe. The second man operates the die which, with the mold, forms the finished shape. The boy places the shapes on a flat tool and carries them to the lehr. In order to obtain the red with selenium, it is essential that a small amount of cadmium sulfide (1 per cent) be added to the raw materials when mixed at the start.

Ruby red may be produced by adding cuprous oxide to a potash-lead glass; on cooling the glass is practically clear; it must be reheated in order to develop the splendid red color. Gold ruby is made by adding gold chloride to potash-lead glass, cooling and then reheating to develop the wine-red color. In the glasses just given the color is due to the colloidal state of the copper and gold; it is in the study of gold ruby glass that Zigmondy made the observation which has led to the present important knowledge of the colloidal state of matter, namely, that the color was due to highly dispersed particles of gold, visible in the ultra-microscope.

Yellow glass may be made by adding selenium or uranium oxide to

soda-lime glass; or by adding 2 per cent cerium oxide and 2 per cent titanium oxide to soda-lime glass, to produce a brilliant light yellow.

The deep blue color of cobalt is well known; it is obtained from cobalt oxide added to soda-lime glass; a greenish-blue is made by adding cupric oxide instead.

Amber glass is obtained by the admixture of a carbonaceous material or iron sulfide in a soda-lime batch.

Opal glass may be made by adding a mixture of calcium fluoride and feldspar to soda-lime glass. Black glass is made by using an excessive amount of pyrolusite and iron oxide mixed.

Green glass owes its color usually to chromium, added as oxide or as dichromate.

Glass Tubing. The manufacture of glass tubing is of particular interest to any student of chemistry. The liquid glass flows out at one end of the tank furnace, over a nozzle-like spout through which compressed air is introduced. The glass is drawn out by a machine and travels a considerable distance; as it travels it is annealed and cooled. When cold enough, it is cut automatically into prescribed lengths. The size of the tubing and the thickness of wall are determined by the viscosity of the glass and by the air pressure. When rods are to be made, the air is shut off. The product of this operation is remarkably uniform as to size and wall thickness. The capillary tubing such as is used for thermometers is drawn in a similar way.

Fused Quartz. In addition to glasses made up of compounds of silica, a glass consisting of silica alone is now available in the form of tubes, rods, plates, and other shapes. Plates of fused silica, or as it is usually called, of quartz, of moderate size, suitable for window panes, are also on the market, although just now at a fairly high price. Quartz permits the ultra-violet rays above 185 millimicrons in length to pass through, hence its great value for health.

Quartz has the property also of expanding only very slightly with heat, so that sudden changes in temperature do not destroy it. It is furthermore resistant to all acids except hydrofluoric acid. For these two reasons it has found application in chemical laboratories and in the industries.

X-ray Glass. Metallic lead absorbs X-rays. Lead in the form of lead silicate in glass retains that property, so that lead glasses have become of importance as shields for the operators of X-ray tubes.

Lamp chimneys are still made in great quantities; they must be resistant to high heat. A low-alkali, high-silica, and high-boric acid glass was found to have the desired properties.

Bulbs for Mazda and other electric lamps are made automatically by ingenious devices.[15]

Light passing through frosted glass is pleasantly diffused; the matt finish which goes by the name of frosted glass is produced by immersion in a bath containing hydrofluoric acid, and saturated with ammonium

[15] *Chem. Met. Eng.*, **39**, 310 (1932).

bifluoride NH_4HF_2. Etching of a design may be done in the same way, except that parts which are not to be etched are covered with paraffin. Electric light bulbs are etched on the inside, by pouring the solution within the bulb.

Fibrous Glass. Fibrous glass is glass reduced by a mechanical process to a flexible, fiber form. On a small scale, it has been made for many years as a curiosity, although not as fine as is done to-day. By throwing a thread of glass, pulled from a heated glass rod, over a rapidly revolving drum, the glass is drawn out into fibers resembling wool or silk; it is possible to weave cloth from such threads. Such fibrous glass is prepared on the large scale to-day, and serves as an insulating glass wool, which is fire-proof, vermin-proof, and has a low thermal coefficient, 0.266 Btu. per square foot area per inch of thickness per hour per °F.[16] It serves for insulation in the side walls, floors, and roofs of dwellings.

On the factory scale there are produced at one time numerous fibers, (a), by directing a stream of fluid glass upon a rapidly revolving refractory disk; (b), by allowing a stream of compressed air to strike at right angles to the hot glass column. A modification of (b) is to allow the stream of glass to flow vertically, and to feed in the compressed air concentrically around the stream. The nozzles delivering the glass are made of platinum.[17]

GLASS BOTTLES

Bottles were formerly made by hand; a worker could produce about 300 bottles a day. This is still done for special shapes, and when the orders call for comparatively small numbers. In such cases, the crew works from a "closed" pot, and an iron blow pipe, with the blow applied from the lungs. For quantity production of standard shapes, automatic bottle blowing machines have been perfected which produce in eight hours 6000 bottles and more.

In a model American plant which produces a blue bottle for a popular pharmaceutical, the furnace (Figure 65) furnishes 27 tons of glass a
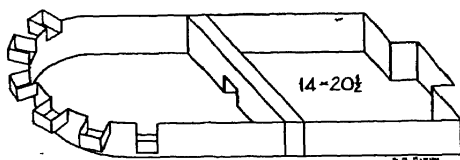
FIGURE 65.—Glass furnace for bottle glass, feeding automatic glass blowing machines. Each of the 6 extensions shown has a machine fed from it.
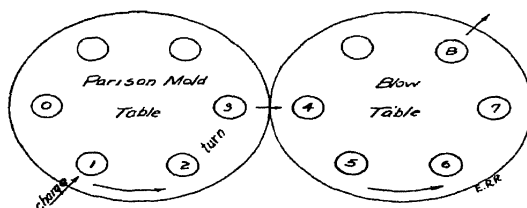
FIGURE 66.—Automatic glass bottle making machine; the two revolving tables.

[16] "The characteristics of fibrous glass," a booklet which can be obtained from the Corning Glass Co., Corning, N. Y.

[17] "The manufacture, processing, and use of glass fibers," by G. V. Pazsiczky, translated from *Glastech. Ber.*, June, 1936, by Dr. Samuel R. Scholes, *The Glass Industry*, **18**, 17 (1937) [11 W. 42, New York].

day. The charge consists of 1000 lbs. sand, 380 lbs. soda ash, 100 lbs. feldspar, 140 lbs. lime (CaO), 800 lbs. cullet; for these 2420 lbs., 1 lb. of cobalt oxide (CoO) furnishes the attractive blue shade. The furnace is fired by oil (72 gallons of oil per ton of glass). From the melting
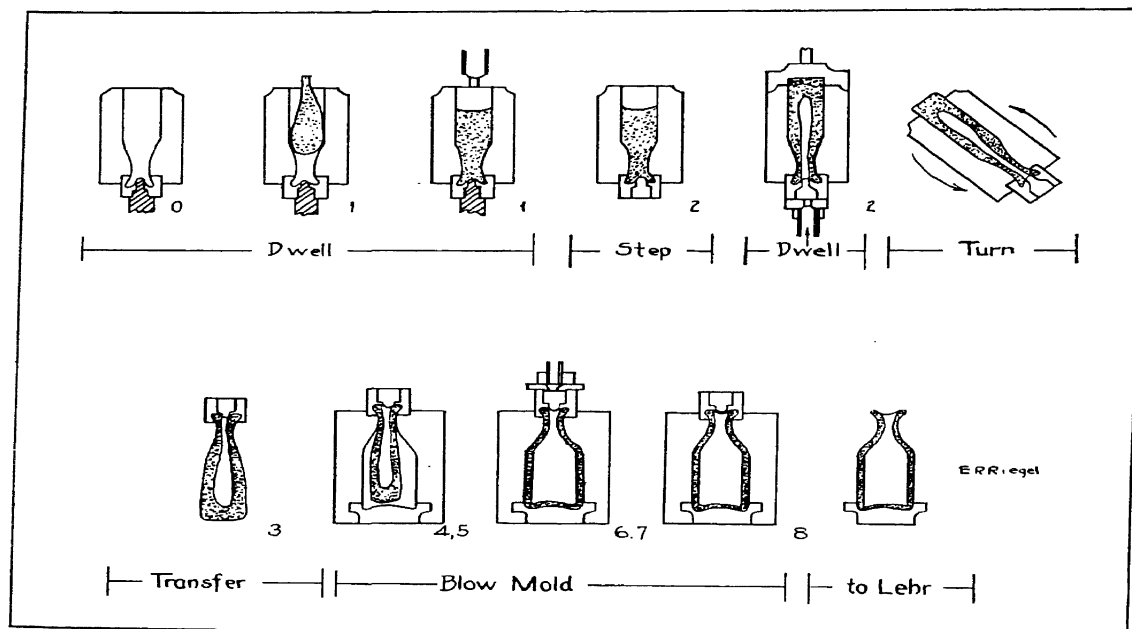
FIGURE 67.—The successive steps in the automatic blowing of a glass bottle. Upper row, the parison mold with its charge; lower row, the blow mold, with charge. No. 3 is the parison. 1. Parison mold arrives empty. Neck plunger comes up. Charged. Compacted by pressure from the top; this forms the finish and gives the neck its final outside diameter and shape (upper half inch of finished bottle). 2. Step to position 2. Counter blow head comes up. Baffle plate comes down. Air blow through neck forms the cavity. 3 and 4. Transfer station. The mold turns between stations 2 and 3. At three, mold halves open, neck mold remains closed, mechanical arm moves the parison by the neck piece to 4. Here, bottom piece comes up. blow mold closes. 5. Reheating time, that is, a fraction of a second is allowed for heat to flow from the inner part of the glass to the outside chilled layer. 6. First final blow. 7. Second final blow, stronger. 8. Take out. Final step. to lehr; mold cooling.

end, the glass passes to the refining end, with 6 extensions, in each of which a clay rod moves up and down, discharging a gob of glass which is cut off by mechanical scissors. The gob drops into a funnel which guides it to the parison mold marked 1 in Figure 66, which shows the two revolving tables of the bottle blowing machine.[18] This figure with Figure 67 will make clear the operation of the machine.

The charging of the furnace is continuous, so that the level of the

[18] For a picture and further description of automatic bottle blowing machines, *see* "Textbook of glass technology," F. W. Hodkin and A. Cousen, London, Constable & Co., Ltd., 1925; New York, D. Van Nostrand Co.
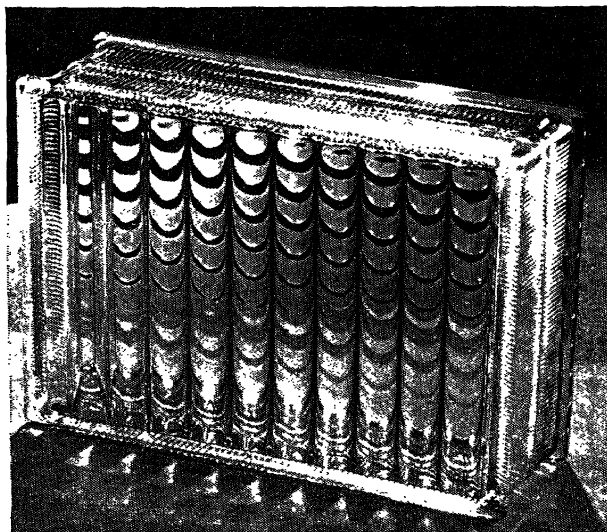
FIGURE 68.—The new Pyrex Glass construction unit, consisting of a closed cell containing air at reduced pressure, and shown as it would appear from the inside of the room; manufactured by the Corning Glass Works, Architectural Division, Corning, N. Y.

glass melt is strictly stationary, insuring regular feed to the blowing machines.

The discharge from the blowing machine is onto a conveyor, from which a mechanical arm picks up the bottles one by one and places

FIGURE 69.—A lighting and ventilating grille of Pyrex, to illustrate Corning-Steuben architectural glass.
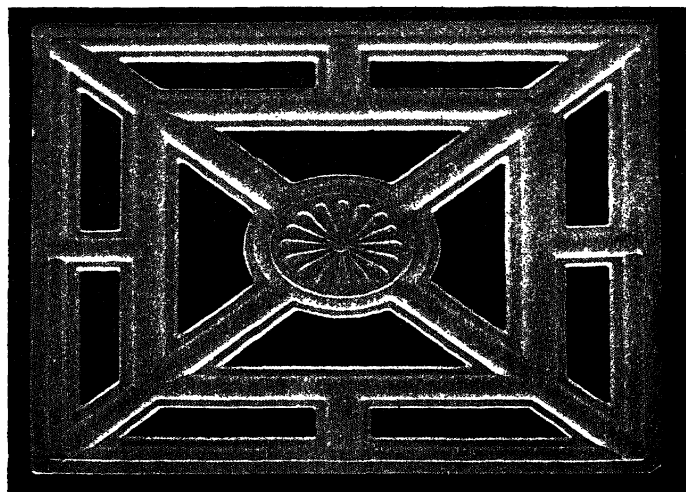
them, spaced irregularly, onto a moving platform which travels through the lehr for the annealing period. The rate of production is 1 bottle in 4 seconds, 900 an hour, for each machine.

Any ordinary bottle shows a thick zone two-thirds of the way down,

marking where the parison ended. A line just under the neck marks the mold for the "finish." There are two lines up and down on each side. The first marks the halves of the parison; the other, the halves of the blow mold. A line near the bottom marks the blow piece at step 4.

Glass Construction Block and Architectural Glass

For several years past, the popular demand for transparent walls have stimulated engineers; there is, as a result, available to-day a Pyrex Glass construction unit, shown in the adjoined figure, measuring $11\frac{3}{4}''$ $\times 11\frac{3}{4}'' \times 4''$. It is a hollow cell, with indentations on the sides, to bind the Portland cement mix which is the cement recommended. At the same time, the highly decorative effects of molded and shaped glass has led to the manufacture of architectural glass, such as lighting panels, ventilating grilles (such as shown adjoined), and panels of great beauty. As a material for construction for the chemical engineer, Pyrex and similar glasses have long proved indispensable.[19]

TABLE 20.—*Selected Items in the Manufactures of Glass and Glass Products, 1935*
(Bureau of the Census)

	Square feet	Value
Window glass	428,938,357	$18,180,053
Plate glass	177,263,478	41,818,918
Wire glass	11,960,829	1,369,144
Obscured glass	14,372,434	1,644,356
Total flat glass		68,266,602
Laminated glass (safety glass)		53,282,938
Mirrors		13,797,368
Cutware		2,759,643
Decorated glassware		1,764,205

Other Patents

U. S. Patent 1,880,540, electric furnace for melting glass and new type of electrodes for such a furnace; 1,920,366, drawing thermometer tubing; 1,838,162, apparatus for producing glass tubing; 2,064,361, spectacle glass composition to give a faint pink shade; 2,056,627, ultraviolet transmitting glass; 1,852,218, apparatus for feeding molten glass; 2,005,494, feeding glass by alternate application of pressure and vacuum; 1,999,562, continuous production of "plate" glass with one rough and one fire-polished surface; 2,012,583, method of manufacturing bottles; 2,030,810, glass forming and gathering machine; 2,045,716, apparatus for casting large telescope disks; 2,053,902, furnace for melting glass; 1,981,636, making lamp bulbs from tubing; 2,034,925, hollow glass building blocks; 1,788,312 and 2,069,130, on glass blowing machines; 1,970,354, on means for feeding glass to the blowing machine.

Problems

1. Compute the total number of square feet of floor area in the furnace described in the text, with the melting end 52 feet by 26 feet included. Where dimensions are missing, scale the drawing, for it is made to scale. Each one inch of height of glass is equivalent to 21.5 tons of glass. What is the apparent specific gravity of the glass melt from this relation? What is the total capacity of the furnace, to a height of 62 inches?

[19] See Pyrex Glass liner in ammonia converter in chapter 6; and compare item in chapter 45.

2. If 60 tons of glass per 24 hours are drawn from the furnace described in Problem 1, how long does any one pound of glass spend in the furnace?

Note: This estimate should be made first on the basis of the calculated capacity, in order to indicate the magnitude of the movement. In reality, only the upper 10 to 16 inches of the melt moves and it is this layer which furnishes glass for the daily withdrawal, so that the rate of movement is faster than first computed. Base other estimates on movement of 10-inch layer, then 16-inch. The higher the temperature, the deeper the layer which moves. The lower immovable portion is colder and hence more viscous.

3. The materials charged into the furnace every half hour are given in the text. The shrinkage due to loss of CO_2 and SO_3, calculated on the basis of pure materials, would be how much? Express in terms of percentage of the total charge.

If your calculated shrinkage is less than 10 per cent, which is the usually observed shrinkage, the difference might be explained on the loss of moisture, alkali oxides, and other volatile impurities.

4. What will be the molecular formula of the glass? (Divide parts by weight by the molecular weight of the oxide, tabulate quotients, and divide by the smallest.)

5. Examine a number of bottles for the telltale lines indicating the steps in the automatic blowing operation as described in the text.

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The industrialist deals not only with raw materials and products of reactions, but also with fuels, steam and electrical power; frequently it is the cost of these rather than the cost of raw materials which determines whether a certain enterprise should be continued or given up. Hydroelectric power is cheaper than steam-generated power; it supplements the latter in a wide territory, not merely locally, for it is feasible to transfer high tension current over distances of several hundreds of miles with almost no loss.

Chapter 12

Fuels, Steam Boilers, Hydroelectric Power, Steam Power, and Production of Cold

There are only a few industrial chemical processes in which fuel is unnecessary; an example would be sulfuric acid manufacture. By far the greater number of processes require fuel, or heat produced by resistance to the electric current. High temperatures, in the neighborhood of 1000° C., are reached by the direct application of fuel, as in the reverberatory furnace.[1] More moderate temperatures, in the neighborhood of 100° C., are conveniently reached and maintained by means of steam in jackets, in coils, or led directly into the reacting mixture (wet steam). Soft coal is the important solid fuel at present; the term includes bituminous and semi-bituminous coal. Anthracite[2] has only slight importance for the chemical and allied industries; soft coal is more abundant,[3] cheaper, and in many cases is preferred because of its long flame. For the manufacture of coal gas, only bituminous or semi-bituminous coal is used; if it be chosen of the coking variety, there is left in the retort another valuable semi-manufactured fuel, coke,[4] the most suitable fuel for iron blast furnaces and similar processes, for its hardness and strength permit it to carry great loads without being crushed. Pulverized soft coal burns like a gas. The liquid fuel is chiefly "fuel oil"[5]; it is burned under boilers, in furnaces of all kinds, to a smaller extent in Diesel engines,[6] internally. Gasoline[5] is a specialized fuel, used for internal combustion motors. The gaseous fuels[7] besides coal gas are natural gas, water gas, producer gas; for the production of the latter, lignite[8] may be substituted for the soft coal usually used.

[1] *Compare* introduction to Chapter 17.

[2] The one important anthracite area in the United States is northeastern Pennsylvania (Scranton, Wilkes-Barre, Mauch Chunk).

[3] There are about 400 anthracite mines and 9000 soft-coal mines in the United States.

[4] Chapter 14.

[5] Chapter 24.

[6] The Diesel engine has no spark plug; ignition temperature is reached by compression (500 pounds).

[7] Chapter 15.

[8] Lignite contains water; the extensive deposits in the West will probably not be worked intensively until coal is exhausted, except for local needs. North Dakota lignite is being mined now (1937) and utilized for making gas and briquet fuel.

A comparison of the heat value [9] of the several fuels is given in Table 21.

TABLE 21.—*Comparison of Heat Values of Various Fuels.*

Anthracite, fixed carbon about 87 per cent	per pound	13,500	Btu.
Bituminous coal, fixed carbon about 60 per cent	" "	14,400	"
Coke, fixed carbon about 92 per cent	" "	12,900	"
Wood, dried	" "	8,000	"
Charcoal	" "	12,800	"
Fuel oil	" "	18,500	"
Kerosene	" "	20,000	"
Natural gas	per cubic foot	1,100	"
Coal gas	" " "	600	"

It is evident from this table that bituminous coal is a high-grade fuel. It occurs in almost limitless quantities in the United States; a recent estimate is three and a half trillion tons, counting all types of coal. The deposits in England [10] are next in importance; next in order would come France, Russia, Germany, and Belgium. Within the United States, western Pennsylvania and West Virginia lead [11]; other eastern and southern States with important outputs are Virginia, Maryland, Tennessee, Alabama. In the middle west, Ohio, Illinois, Indiana, Iowa, Missouri, and North Dakota have important coal resources; further west, Wyoming, Colorado, Utah, New Mexico, Oklahoma and Washington. Coal is generally agreed to be of vegetable origin.[12]

The methods of mining differ greatly. In the Pittsburgh district, a five-foot seam near the surface, so that no shaft is necessary, but merely inclined tunnels, is mined in the following way: "Rooms," 250 feet deep and 20 feet wide, are marked out and the coal removed, leaving a wall between the chambers; a coal pillar must also be left around any oil-well casing, reaching to the oil-bearing strata underneath. Within the room the cutting of the coal is done by electrical machinery and dynamite. The cutter, a low steel truck carrying two motors, travels on the narrow-gauge tracks in the tunnels to the room ready for a cut; within the room, it is hauled on timbers, pulling itself by means of a steel cable, drum-wound, looped around a temporary brace jammed between the ceiling (the height of the room is the height of the seam,

[9] British thermal unit, the heat required to raise 1 pound of water 1° F.; it takes 4 Btu. to equal 1 large Calorie, the heat required to raise one kilogram of water 1° C. (at 18° C.).

[10] The British coal fields are: a. The southern, including South Wales and Monmouth, and partly under the sea; the coal is of all varieties, bituminous, anthracite, and intermediate; the seams are rarely over 3 feet in thickness, usually less. b. The central fields, North Wales, Yorkshire, Derbyshire, which yield coking bituminous. c. The northern fields, Scotland, Durham, which give good coking coal. The Ruhr district gives mainly coking bituminous. The basin in Northern France adjoins and in fact is part of the Belgian field; the coal is bituminous of all varieties. The Saar Valley coal is non-coking.

[11] Production in millions of tons (1934) (Bureau of Mines) W. Va., 98.1; Pa., 89.8; Ill., 41.2; Ky., 38.5; Ohio, 20.7; Ind., 14.8; Va., 9.4; Ala., 9.1; Col., 5.2; Wyo., 4.4; Tenn., 4.1; Iowa, 3.7; Mo., 3.4 Kans., 2.5. Total bituminous 359.37 million tons (1934) with value $1.75 a ton. Anthracite 51 milion tons, Pa., 1935. 1931, grand total for all coals, 437.64 m. tons; for 1929, grand total 534.99 m. tons. 1930 price, bituminous, $1.70; anthracite, $5.

[12] The very interesting and rather satisfactory theory that coal is a petrified residue of prehistoric fruit of various kinds, rich in oily matter, sugar, starch and albumen, has been advanced recently. Such fruit would stand in the same relation to ours as the dinosaurs to our present-day animals. Amber is an example of petrified gum, whose history we know. Private publication by Dr. Samuel Braun, Beregszasz, Czechoslovakia, 1926. Petroleum had its origin, in this theoretical consideration, in the oil of ripened olives the size of melons, which flowed into cavities in the earth's crust; by later geologic events, these chambers were sealed.

5 feet) and the floor. The cutter has a 9- or 10-foot tongue close to the floor; an endless chain carrying short stout knives travels along its edges, actuated by a sprocket wheel driven by the motor. Power is taken by a flexible drum-wound cable from the copper lead in the tunnel. The tongue is allowed to penetrate into the wall close to the ground, cutting away the coal. The fine coal is swept out by the knives; during this

FIGURE 70.—Curves showing the relative importance of the several sources of energy over a period of years. Curve 1, coal; 2, petroleum oil and natural gas; water power. 3. The sharp drop in coal and equally sharp rise in oil and gas is well shown, to 1932; since then, the lines are roughly parallel. The water power is converted into its coal equivalent by accepting a unit consumption of 4 pounds of coal for each kilowatt hour. (Figures from Bureau of Mines, Coal Economics Division, Feb. 10, 1937.)
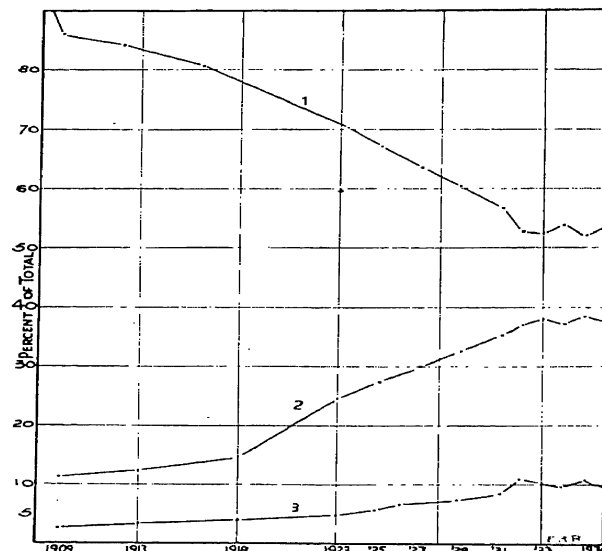
operation, the cutter is hauled close to the wall by the cable, and this pressure forces the knived belt of the tongue inward. With the tongue all the way in, the belt continues running, and the cutter is slowly moved, again by its own cable, from one side of the room to the other, clearing a horizontal space 6 inches high, 9 feet deep, and 20 feet wide. The cutter is now removed from the room by its two operators, and the miner takes charge; two or more holes are drilled into the coal, 5 feet deep, and set close to the ceiling; they are filled with dynamite and fired. In nearly every case the whole block, 5 feet by 6 feet by 25 feet, is tumbled down.[13] The miner with his helper loads the coal on the low mine cars and these are pulled out by an electric locomotive, at high speed, to the breaker house or tipple where the coal is crushed somewhat, freed from fines, and loaded by gravity (the breaker house is elevated) into railway cars.[14]

For household use, anthracite is preferred to soft coal,[14a] at least in

[13] The lay-out of the room is so planned with reference to the structure of the coal that the blast finds the lines of weakness, and as a result the coal falls forward with minimum blasting.

[14] The Primrose Mine, Carnegie Coal Company, Pittsburgh, Pa.

[14a] In North Dakota, which possesses no other fuel than lignite, this low-grade material is being mined, distilled in special patented retorts, furnishing gas to municipalities, and briquet fuel to the state and to neighboring states. The development of by-products is under intensive study.

the areas not too far from western Pennsylvania. Its use has been made more attractive by the application of a spray of calcium chloride solution, which prevents the formation of dust.

"Blue coal" is anthracite sprayed with a suspension of finely divided ultramarine or "Celestial Blue" in water, followed by partial or complete drying.[15]

The distillation of coal is presented in chapter 14; its hydrogenation, in Chapter 24.

STEAM BOILERS

Stationary boilers fall into two classes; water-tube boilers, in which the water is inside the tubes, the fire gases on the outside, and fire-tube boilers, in which the fire gases pass inside the tubes, while the water
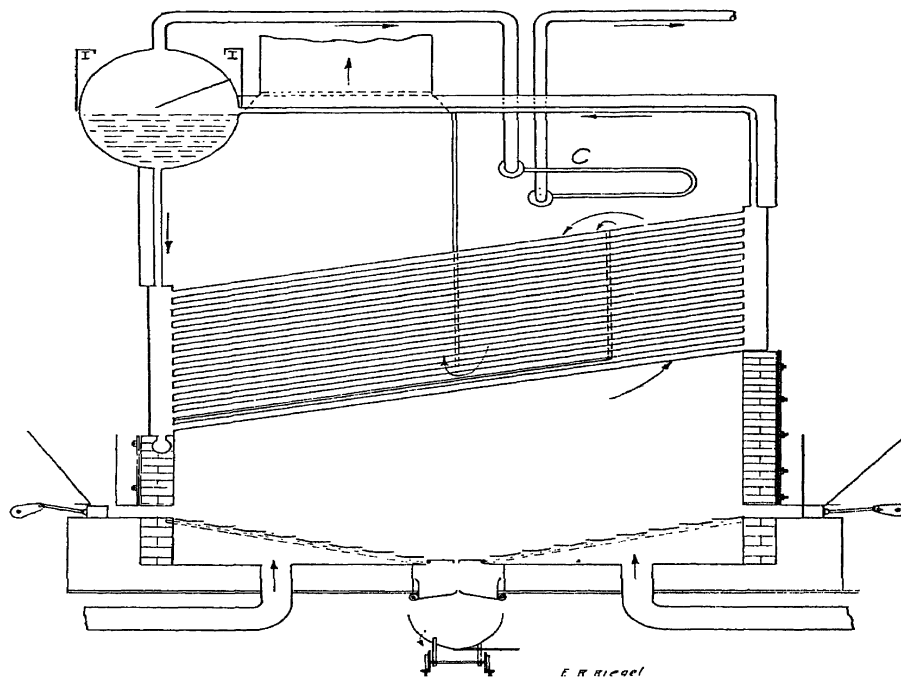
FIGURE 71.—A water-tube boiler, with superheater at *C*. The circulation of the water and steam is shown, also the entry for the forced draft under the grate, the method of removing ashes, and the travel of the fire gases.

is on the outside. Either type has also one main drum or several drums which carry the greater part of the water. Locomotive boilers and most marine boilers are fire-tube boilers.

[15] U. S. Patent 1,688,695, to Dr. Gustavus J. Esselen; no adhesive is required.

The water-tube boilers are more efficient, safer, and are used for medium pressures, such as 200 and 275 pounds steam pressure per square inch; their development is more recent than that of the fire-tube boilers. The Babcock and Wilcox, the Stirling, and the Heine boilers are water-tube boilers. In Figure 71, it may be observed that the fire gases strike
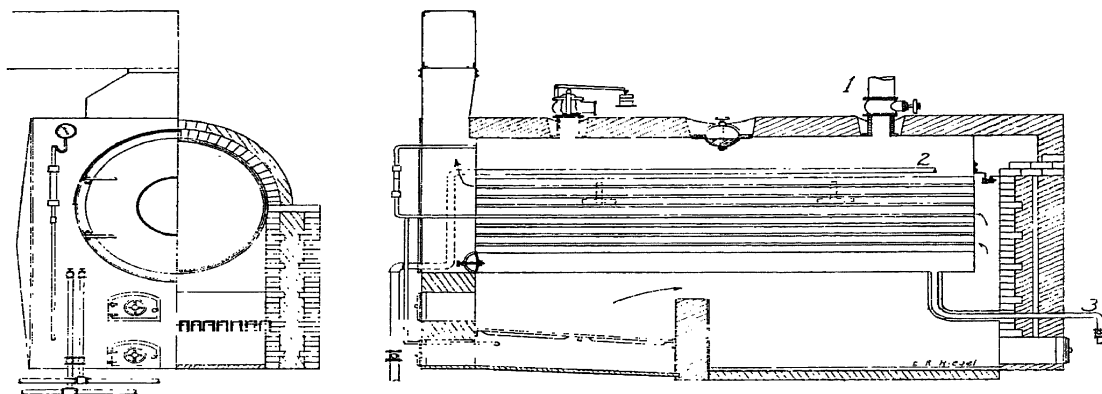
FIGURE 72.—A fire-tube boiler, with hand-fired grate and natural draft; the steam leaves at 1; the feed water is delivered at 2; the blow-off cock is 3.

the tubes at right angles; while in the fire-tube boilers, the path of the fire gases is parallel to the tubes. The exchange of heat is more rapid with the former construction. An illustration of the fire-tube boiler is also given (Figure 72); it is cheaper in first cost, well suited to smaller plants, particularly for pressures of 60 pounds per square inch.[16] Both illustrations furnish a number of details.

The material for the drums is mild steel, usually one-half inch in thickness, riveted; the tubes are rolled or spread to fit. In the superheater, shown in the water-tube boiler sketch, the steam, after it has left the boiler system proper, is passed through a nest of pipes placed in the flue gases, where its temperature is raised 100 or more degrees above the boiler steam temperature. This treatment raises the work value of the steam, and is important for steam used in engines and turbines; for steam used for heating coils and jackets, such as the chemical engineer requires, it is less important, for it does not raise the heat value of the steam by very much.[17] For this reason it is common practice, in plants having high-pressure steam, to use superheated steam in a single-stage engine working between 275 pounds and 40 pounds, and to use the exhaust steam for heating. In general, exhaust steam from pumps, engines, and compressors is

[16] If the steam must travel a long distance (2000 feet for instance), high-pressure steam is preferred, for smaller pipes will transport the same amount as larger pipes carrying low-pressure steam.

[17] Sixty-pound saturated steam has a heat content of 1177 Btu. per pound of steam; 60-lb. steam with 100° F. superheat has a heat content of 1227 Btu. The temperature of steam rises with rise in pressure; 60-lb. steam is 293° F.; 100-lb. steam 328° F.; 200-lb. steam 382° F.; the pressures are absolute. Marks, "Mechanical Engineers' Handbook," New York, McGraw-Hill Book Co.

collected in steam drums and fed from here to heating coils, sending fresh steam from the boiler into the drum only when the supply of exhaust steam is insufficient.[18]

A high pressure steam boiler for a chemical plant, with a high degree of economy of operation and reliability for continuity has been described [19] and illustrated. Three such boilers generate 260,000 pounds of steam per hour at 250 pounds pressure.

High Pressure Steam. Very much higher pressures are developed in water-cooled furnaces, that is, in water-tube boilers having a part of the tubes set in fire-bricks and forming the walls. Within the furnace space so provided, pulverized coal or oil is burned, with the development of high temperatures which would damage the walls were they not water cooled. The water is vaporized at a high rate, and the pressures developed are of the order of 1500 pounds per square inch. An example of such an apparatus is the Bailey water-cooled furnace manufactured by the Babcock-Wilcox Co. Distilled water, absolutely free from mineral matter as well as from dissolved gases is the working substance for the high pressure boilers.

High Temperature Vapors. For the development of high temperatures, diphenyl boilers, or diphenyl oxide boilers are in use. With a pressure of 144 pounds per square inch (gage pressure), a temperature of 750° F. (399° C.) is attained. The pressure is moderate, and the temperature may be maintained constant without any difficulty.

Mercury vapor has been used as the working substance in a boiler and turbine for several years, and on the experience gained thereby, two new improved mercury vapor systems have been installed at Hartford, Conn., and an outdoor station at Schenectady.

In the original 1928 installation, an overall thermal efficiency of 33 per cent was obtained over the year. In the new ones, it is expected that 36 per cent will be reached. Mercury in a porcupine boiler, cylindrical with finger-like extensions on its lower part, preheated, is vaporized by direct heat from an oil burner; a temperature of 885° C. (1625° F.), under a pressure equivalent to a column of liquid mercury 17 feet high, is recorded. The mercury vapor drives a turbine; the exhaust vapors pass to a steam boiler, in which 400 pounds of steam is raised. The steam is superheated and drives a turbine also.

Boiler Rating. Boilers are rated in boiler horse powers. Generally 10 square feet of heating surface, shell and tubes, are considered equivalent to 1 boiler horsepower; such a surface evaporates 34.5 pounds of water at 212° F. to steam at the same temperature (33,475 Btu.) per hour. This method is being gradually displaced by a rating in terms of the pounds of water a boiler evaporates per hour.

Water Softening. In order to prevent or at least minimize scale formation, the water fed to the boiler must be freed from dissolved calcium and magnesium salts. For water with carbonate hardness, containing

[18] The regulation is by means of a Locke damper regulator.
[19] "Cheaper power for the chemical industry," W. S. Johnston, *Ind. Eng. Chem.*, **23**, 476 (1931).

calcium carbonate held in solution by carbon dioxide, milk of lime may be added, which will cause the precipitation of calcium carbonate. For water with non-carbonate hardness, containing calcium sulfate, soda ash is used. The treatment is best performed in separate vessels, and the water filtered by percolation through sand; or the softening chemical is sent directly into the boilers. In either case, the boiler must be blown once or more often per day, for the soluble salts accumulate, and such solutions cause "priming," and other difficulties. By opening the blow-off cock, shown in Figure 72, a portion of the contents is removed and replaced by cleaner water. The task of supplying clean water to the boiler is lightened by returning all clean condensed steam to the boiler room. The boiler feed water is generally preheated.

Recent work in the Bureau of Mines has led to the recommendation that trisodium phosphate be used for conditioning boiler water. The muds formed are more soluble, or as soluble, in the very hot water and therefore do not form a scale, but float so that they can be removed by a special filtering installation. It has been shown in the course of this work that soda ash solutions tend to render steel brittle.

The carbonate hardness may also be removed by heating in a vessel with trays, having provision for the escape of the carbon dioxide driven out. The calcium carbonate precipitates on the trays, which are removed and cleaned periodically. Non-carbonate hardness is not removable by this method.

Another way to soften water is to pass it, cold, over zeolites,[20] as described in the next chapter, where the subject of water softening is presented in more detail.

Mechanical Stokers. Hand shoveling of coal is still practiced, and in smaller plants has much in its favor. In larger plants, mechanical stokers are used in order to save labor, but also to prevent smoke and to give a more uniform fire. The Taylor stoker has an inclined stationary grate; each "retort" has two rams or plungers, one above the other, and a number of retorts make up the stoker. Between the retorts a step-like surface is provided, with holes at each step through which the forced draft enters the fire. The upper ram moves fresh coal under the blanket of fire, so that the heat causes the volatile portions to pass out and over the bright fire where they are consumed, thus preventing smoke. The lower ram pushes the bed of coal outward and downward toward the dumping platform. The motion of each ram is slight, only a few inches, and the strokes are 1 in 2 minutes (adjustable). The Taylor stoker belongs to the class of underfeed stokers.

The Roney stoker is also an inclined stoker, with bars running the full length of the fireplace and moving separately, at intervals, so that the blanket of fire advances slowly downward toward the dumping bars; it belongs to the overfeed stoker class. Still another mechanical stoker is the chain grate, consisting of an endless belt as wide as the fireplace, moving very slowly toward the rear of the boiler. Fresh coal is fed by

[20] *Ind. Eng. Chem.*, **19,** 445 (1927).

FIGURE 73.—The application of water to a turbine wheel; cross-section through the forebay and terminal basin of the hydraulic canal and tunnel, penstock cut in the rock, Johnson regulating valve, draft tube for escaping water, and generator. Niagara Falls Power Company Plant 3B, in the gorge. The difference in levels averages 217 feet. (By permission.)

gravity to one end of the grate which carries it into the hot zone; at the turn, the ashes are dumped. The chain grate stoker operates with natural draft.

A flue gas analysis indicates if proper burning takes place; no carbon monoxide should pass out as such, but should be burned to carbon dioxide. The excess of air should be small. Such analyses are made by means of the Orsat apparatus, carrying a measuring bulb and absorption pipettes.[21] This control is used constantly, but is more important with hand firing than with mechanical stokers. The temperature of the stack gases is 500° to 600° F. (260° to 315° C.).[22] If the load on the boilers is not
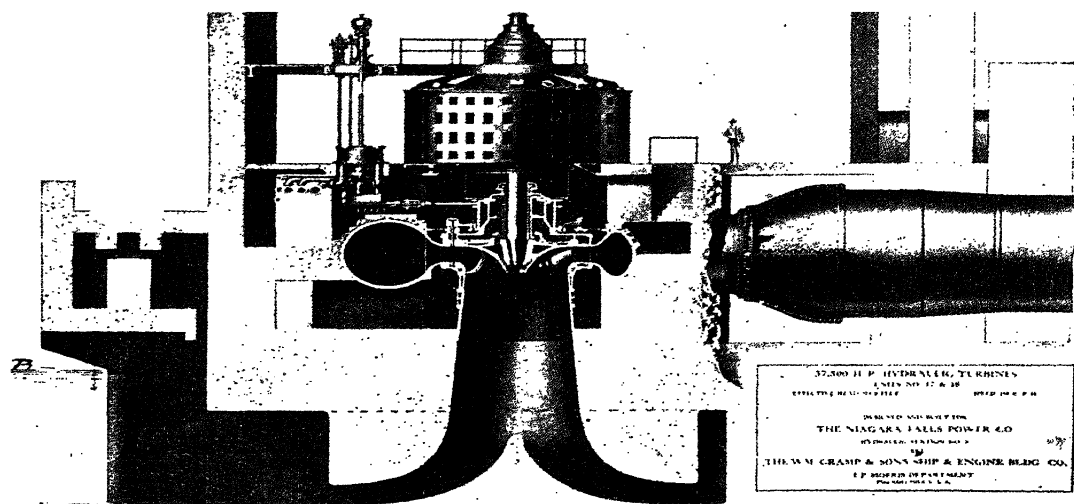
FIGURE 74.—Assembly of generator, water wheel and casing, and draft tube for the escaping water. The water from the penstock, at right, reaches the casing in the wider part first. Mean level of river shown at *R*. Niagara Falls Power Company Plant 3B. (By permission.)

steady, that is, if steam is drawn off irregularly, it is important to alter the intensity of the fire by altering the draft; in case of hand firing, with natural draft, a Locke damper regulator is a simple equipment which responds quickly. Automatic carbon dioxide recorders are on the market.[22a]

Even mechanical stokers are classed now with the developments of a past age; the present day method of applying coal energy to the boiler is by means of powdered coal. A heavy duty pulverizer is set close to the boiler, and is swept by a blast of air which carries the fine coal (through 200 mesh) into the burner, where it burns like gas or oil. There

[21] There are 3 absorption pipettes: *a* alkali solution for CO_2; *b* alkaline pyrogallol for oxygen; *c* ammoniacal cuprous chloride for CO.

[22] For a complete heat balance sheet, see Marks, "Mechanical Engineers' Handbook," New York, McGraw-Hill Book Co., 1916, p. 898.

[22a] For example the Ranarex, described in Chapter 46.

accumulates a melted slag in the bottom of the boiler setting, and this is drawn off by tapping just as a blast furnace is tapped. To complete the picture of a first class utility installation making electrical energy from coal; each boiler is 70 feet high; it evaporates 620,000 pounds of water per hour; the steam pressure is 450-475 pounds, and the superheat is 680-750° F. (360-399° C.) [22b] Each boiler has 1,320 tubes (water tubes), 4 inches in diameter, and 24 feet long. The water is all previously distilled. The steam is applied to a turbine generator, as stated further on. As to efficiency, such a plant as this has a consumption of 0.95 pound of coal per kilowatt hour generated.

HYDROELECTRIC POWER

The utilization of water power to its full capacity is a modern development which had to wait until the science of generating electric current was sufficiently advanced. By means of the electric current, the enormous quantity of power developed in one spot, at a waterfall, for instance, may be distributed over a wide area, many miles away. If water power had
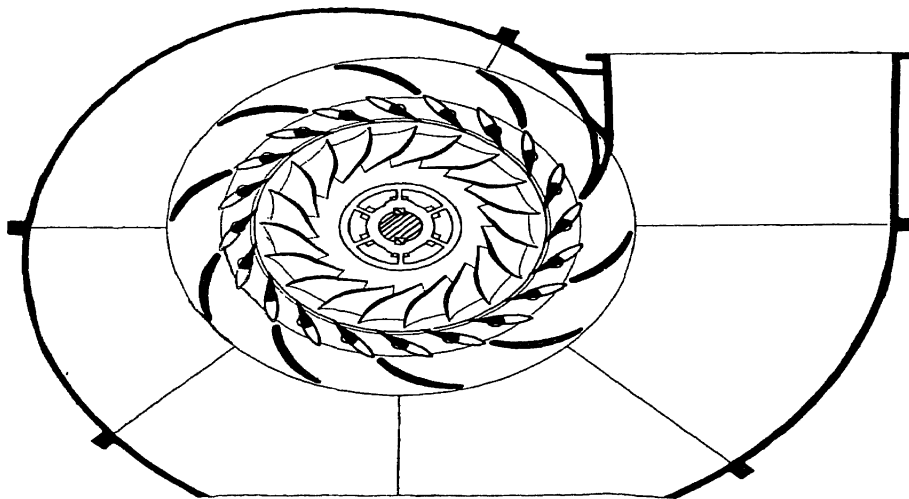
FIGURE 75.—Horizontal cross-section through water wheel, wicket gates, guide vanes, and casing. The water wheel is 16 feet in diameter, and its speed is 107 r.p.m. The water escapes downward. Niagara Falls Power Company Plant 3B. (By permission.)

to be used as mechanical power (rope and belt drives), the present-day developments would not exist. Hydroelectric power is important because it is independent of a supply of coal. The cost of installation of a hydroelectric power plant is much greater than the cost of installation of a steam power plant, but the running cost is lower.

[22b] Buffalo, N. Y., Huntley, Niagara Hudson System.

Water power is transformed into electrical power by applying the water to a wheel (turbine), which carries on the same shaft the pole pieces, for example of an alternating-current generator; the armature is stationary. The opposite arrangement is used less often. At Niagara Falls, the voltage is 12,000; for distance transmission, this current is raised to 60,000 volts in oil transformers. Direct current is produced from the alternating current by applying it in the separate manufacturing plants to the motor of a direct-current generator. Water power may also be transformed directly to direct current.

TABLE 22.—*Capacities for the Major Hydroelectric Power Projects in Kilowatts.* (*Estimated, June, 1937*)

	Present installed capacity	Ultimate installed firm power
Niagara river, at Niagara Falls	986,000 (Can.)	
	561,000 (N.Y.)	
Boulder Dam, Colorado river	115,000	1,000,000
Grande Coulée, Columbia river		2,520,000
Bonneville, Columbia river		688,000
Wilson Dam, Tennessee river	261,400	620,000
Norris Dam, Clinch river	132,000	235,000
Pickwick Landing Dam, Tennessee river	96,000	288,000
Wheeler Dam, Tennessee river	90,000	612,000
Chickamauga, Tennessee river	72,000**	210,000
Guntersville Dam, Tennessee river	68,000***	134,000
Conowingo, Susquehanna river	378,000	594,000
Total potential capacity for the United States*..		80,000,000
Total installed capacity, U. S.*	20,000,000	

The flow of the water over the year is steady for the Niagara river, fairly steady for the Colorado and Columbia rivers; it fluctuates widely for the Tennessee river and the Susquehanna river. In installed capacities, the states rank as follows* for 1936: California, 15.2 per cent of total; New York, 11.7; Washington, 6.4; North Carolina, 6.1; Alabama, 5.4; South Carolina, 5.0; Maine, 3.8; New Hampshire, 3.6; Pennsylvania, 3.5; Georgia, 3.5.

* Geological Survey, January 6, 1936.
** To be completed in 1939.
*** To be completed in 1938.

The penstock brings the water from the upper level to the level at which the waterwheel is situated, and delivers it to a spiral casing surrounding the wheel. It enters the buckets of the wheel and escapes downward, best through a draft tube in which suction is developed which acts on the wheel by decreasing what might be called the back pressure. In the latest plant at Niagara Falls, the penstock is cut into the solid rock, lined with concrete (*see* Fig. 73). The second illustration (Fig. 74) indicates the relative location of penstock, casing, water wheel and generator; while the third (Fig. 75) gives details of the casing and water wheel. The generator shown develops 37,500 horsepower or 28,000 kilowatts (27,964).

The capacities for the major hydroelectric power projects are shown in Table 22.

Steam-Generated Power

Steam is not usually generated from electric current, but a practical method for such generation has been described.[23] The opposite process, however, the generation of electrical power from steam, is a universal one. A steam plant may be installed at lower first cost than a hydroelectric power plant; it may be installed at any point to which coal may be hauled; it has the third advantage of being flexible, that is, it may be shut down in part or in total for certain hours in the day. Hydroelectric power on the other hand cannot be shut down economically, for the raw material, the flowing water, passes at the same rate over the 24 hours. In the Buffalo district, the basic load, which is even over the 24 hours, is furnished by hydroelectric power; the morning and evening peak loads are carried by a large steam plant, of over 400,000 horsepower. By this combination, economical use of both sources of power is made.

It was estimated in 1936 and 1937, that the initial investment for a steam plant is $83 per kilowatt hour to be produced, and for a hydroelectric plant, $250 per kilowatt.

The cost of coal at the mine is about $2.00 per long ton (1937); to this must be added the cost of freight, which to many large centers, equals and even surpasses the original cost. For this reason steam plants situated at the mines have a great advantage, and can manufacture electric current at a lower cost. This current may then be transmitted over high-tension lines as the hydroelectric power is. Such steam plants are called mine-mouth plants.

The modern method is to superheat the steam and to apply it to a steam turbine with horizontal shaft, which carries the field of an alternating-current generator. For example,[24] a Curtis steam turbine with 13 or 16 stages may be used. Each stage consists of a turbine wheel with numerous curved copper buckets about 3 inches long and three-quarters of an inch wide, set radially near the periphery, and a stationary piece with similar copper pieces set in the opposite sense; these act as guides for the steam and send it into the curve of the rotating buckets. The speed is 1500 rpm. and the capacity of each generator varies from 20,000 to 35,000 kilowatts; the voltage is 12,000. The steam entering the turbine is 675° F. (357° C.); the last stage leads to a surface condenser, so that the pressures are 260 pounds at entry, and 12 pounds below atmosphere at exit (in absolute pressures, 274.5 and 2.5 respectively), a range of 272 pounds.

Cold Production or Refrigeration

Temperatures just above the ice point, and below, are reached with the aid of chemical refrigerants chiefly. Arranged in the order of their importance, the substances used are anhydrous ammonia, carbon dioxide, sulfur dioxide, methyl chloride, ethyl chloride, and paraffin hydrocarbons.

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[23] "The electric steam generator," an article by Horace Drever, *Ind. Eng. Chem.*, **14,** 923 (1922)
[24] Buffalo General Electric Steam Plant.
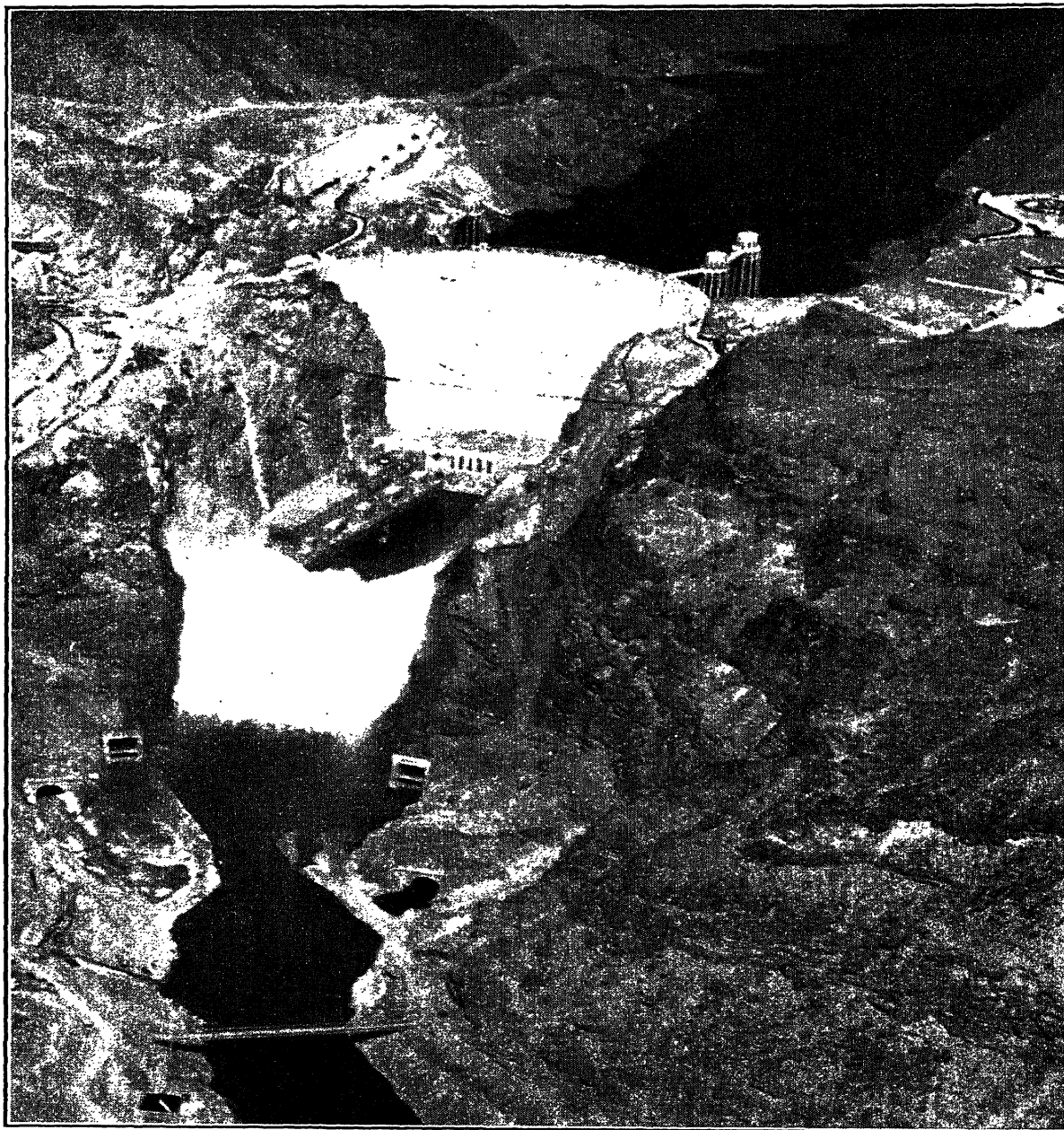
FIGURE 76.—Boulder Dam, as seen from the air. The Colorado River flows toward the reader. *Upper left,* Nevada spillway; *upper right,* Arizona spillway. Just up-river from dam, the four intake towers feeding power houses in front of dam, at the lower river level. The dam is 726 feet high. (U. S. Bureau of Reclamation, Department of the Interior.)

Ammonia is by far the more commonly employed refrigerating agent; it is used for ice manufacture, for cold storage of meats, fruits, vegetables and dairy products, and for general refrigeration.[25]   Carbon dioxide is a somewhat less efficient agent; it is used instead of ammonia when the odor of the latter in case of leak would be objectionable, for instance in hotels, in some hospitals, and on board ship.   It is used also for temperatures below those which ammonia can furnish.   Sulfur dioxide is the most generally used "working substance" for household refrigerators; for the same purpose, but less generally, methyl chloride is utilized.   Paraffin hydrocarbons, ethane, propane, butane, and isobutane, are used only in special cases.   With any of the agents listed, the method consists of compressing the gas sufficiently so that on cooling with ordinary cooling water, it will liquefy; then sending the liquid, still under pressure, to an expansion valve leading to coils in which the expansion takes place; heat is abstracted from the surrounding liquid or room, to make the expansion of the liquid to gas possible.   The expanded gas is compressed, and sent through the system again.   The same material serves over and over; only the losses due to leaks must be replaced.

The boiling points at atmospheric pressure for the various working substances follow:[26]

Ethyl chloride C_2H_5Cl	+	55° F.	or + 12.5° C.
Sulfur dioxide SO_2	+	14	or − 10
Methyl chloride CH_3Cl	−	11	or − 23.9
Dichloro-difluoromethane CCl_2F_2	−	21.6	or − 29.8
Anhydrous ammonia NH_3	−	28	or − 33.3
Propane C_3H_8	−	49	or − 45
Carbon dioxide CO_2	−	108.8	or − 78.2

For an ammonia system, cast-iron, wrought iron, and steel are used; copper and brass are avoided.   The essential parts for a refrigerating plant using brine as an intermediate cooling substance are shown in Figure 77.   The pressures are moderate; on the high pressure side, the gas is compressed to 155 pounds, with a temperature of 210° F. (99° C.). The gas is cooled to 75° F. (24° C.), with the pressure maintained near 155; it liquefies and collects in a receiver.   A small stream is sent through the expansion valve (an ordinary iron globe valve) to the low pressure coils, where the liquid turns to gas, absorbing heat from the brine.   The brine is circulated through a suitable system of pipes (pump).   A temperature of 15° F. (−9.4° C.) for the brine is usually reached.   The gas returns to the compressor with a pressure of about 20 pounds.

The sources of ammonia are discussed in Chapters 6 and 14.

In the liquid carbon dioxide refrigerating system, the pressure on the high-pressure side (condenser) is 1000 pounds; on the low-pressure side (expansion coils) 300 pounds per square inch.   The condenser tem-

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[25] Wax is separated from oil by ammonia refrigeration (Chapter 24); for the liquefaction of chlorine, either ammonia or carbon dioxide may be used (Chapter 5).

[26] For explosion limits and physical properties other than boiling point consult "Properties of Refrigerants," Circular 2, 1926, American Society of Refrigerating Engineers, 37 West Thirty-ninth Street, New York.

perature must be as much below 88° F. (31.1° C.), the critical temperature,[27] as possible.

THE SOURCES OF CARBON DIOXIDE

Carbon dioxide is used commercially as a gas (soda ash manufacture), compressed as a liquid in steel cylinders (soda fountains, for refrigeration, and as convenient source of the gas), and as the solid. It is obtained from (1) the combustion of coke; (2) the calcination of limestone; (3) as a by-product in syntheses involving carbon monoxide; (4) as a by-product in fermentations; (5) by the action of sulfuric acid on dolomite; (6) from wells.[28] Gas from any one of these sources may be made into the gas, liquor, or solid form of carbon dioxide.
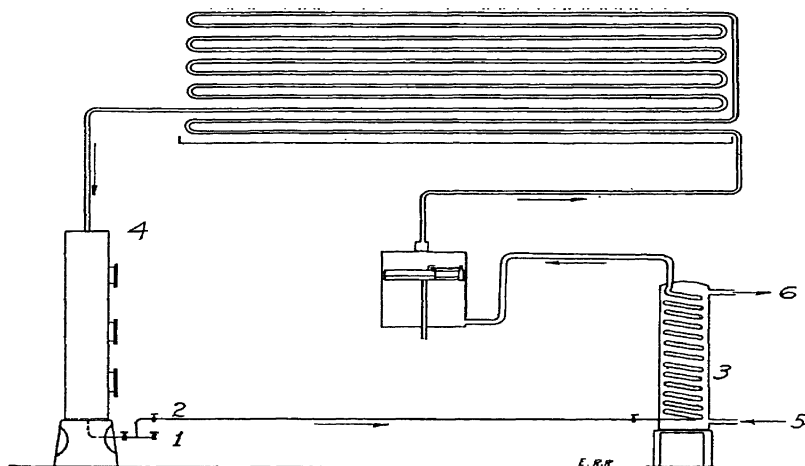
FIGURE 77.—Refrigerating plant with ammonia as working substance. Fresh supplies from purchased cylinders are introduced at 1 into the receiver 4; the liquid and is used over again. The brine enters the cooler and reaches the compressor and from there the condenser. The liquefied ammonia collects in receiver 4 and is used over again. The brine enters the cooler 3 at 5, and leaves at 6; brine circulation not shown.

The utilization of the carbon dioxide in the combustion gases of coke involves the alternate formation and decomposition of alkali bicarbonates in solution. Hard coke is burned under boilers, and the fuel gases so regulated that a maximum content of carbon dioxide, 16 to 17 per cent, is obtained. The gases enter a scrubber (tower) packed with limestone to remove sulfur compounds and fed with water to cool the gas and arrest the dust. The cold gases enter the absorber, a tower packed with coke

[27] The critical temperature is the temperature above which the gas cannot be liquefied, no matter how great the pressure; *see also* footnote 31.

[28] "Solid carbon dioxide from Mexico," James Welford Martin, *Ind. Eng. Chem.*, **23**, 256 (1931).

down which a solution of potassium carbonate passes; carbon dioxide is absorbed, and the saturated solution is run to a boiler where the absorbed gas is liberated by heat. It is under this boiler that the coke is burned. The operation is continuous; charged solution flows in constantly, while the spent liquor is run off constantly. By means of an interchanger, the outgoing liquor heats the incoming liquor to some extent. The outgoing liquor, cold, returns to the absorber. The gas from the boiler is very pure. It is dried in a calcium chloride tower, and compressed to 100 atmospheres, at which pressure it liquefies at ordinary temperatures. (*See* Fig. 78.)

The other sources are presented in their proper places, except source (5), which is unusual. In Georgia,[29] a deposit of dolomite is mined, and the crushed rock treated with sulfuric acid in carbonators provided with a cover and gas outlet. The residue in the carbonators is a solution of
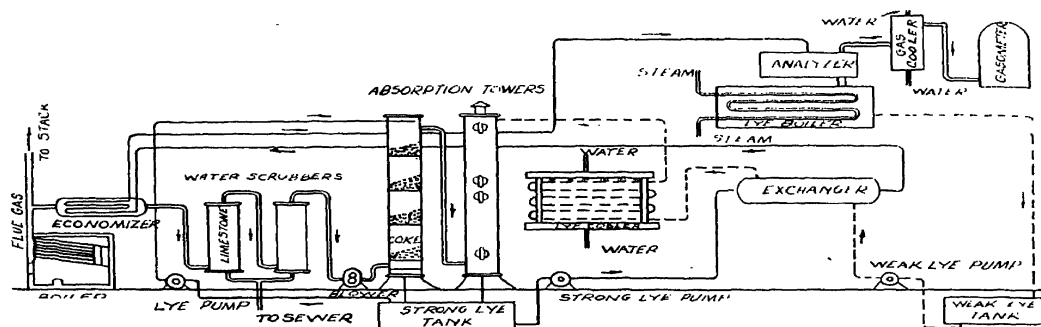
FIGURE 78.—Diagrammatic flow-sheet for the absorption of carbon dioxide in the fire gases from burning coke. The gas dissolves in a strong lye solution, from which it is driven out by heat, giving 100% CO_2 gas. (Courtesy of the Frick Company, Waynesboro, Pa.)

magnesium sulfate, in which calcium sulfate is suspended. By keeping the solution on the acid side, no detectable quantity of calcium salt dissolves. The solution is made into Epsom salts $MgSO_4 . 7H_2O$, a laxative, and a material for the leather industry. The carbon dioxide is compressed to the liquid and used for beverages.

In addition to the uses which have been mentioned, carbon dioxide serves as a chemical in the manufacture of salicylic acid, white lead, and other products. In fire extinguishers, of the wall type, a supply of acid in a separate container is spilled onto lumps of soda ash or bicarbonate; the generation of the gas is so rapid that pressure develops in the container. The gas does not burn, nor does it support combustion, and being heavier than air, it forms a blanket over a burning object. The use of carbon dioxide gas as a fire-extinguishing agent has been extended in the "firefoam" system, in which the gas is held longer at the burning surface by a foam from a soap or alum solution; soap solution and gas are ejected at the same time from the nozzle.

[29] "Manufacture of carbon dioxide and Epsom salts," W. P. Heath, *Ind. Eng. Chem.*, **22, 437** (1930).

Solid Carbon Dioxide

One of the new refrigerants obtainable in commercial quantities is solid carbon dioxide. It is supplied in block form resembling the familiar artificial ice cake. Its uses are similar to the uses of ice, but it functions without melting, and without producing drips; it vaporizes, and leaves only a gas, which may be easily vented, so that it has received the rather apt name of dry ice. Its manufacture will be described for the case of a plant particularly well situated with regard to its source of raw material.[30]

Pure, liquid carbon dioxide under a pressure of 1000 pounds and at a temperature of 70° F. (21° C.), is delivered to the plant by a pipe system. It is sent to the "evaporator" (Fig. 79), where its pressure is reduced

FIGURE 79.—The "evaporator," in which the liquid carbon dioxide is formed and stored.
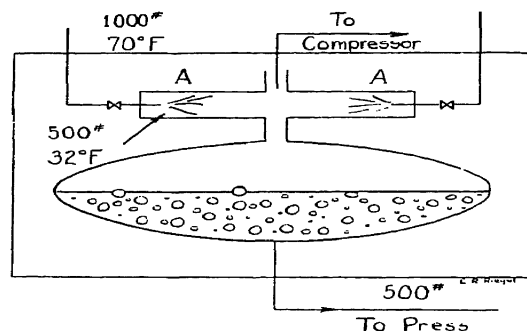
to 500 pounds, with a simultaneous drop in temperature to 32° F. (0° C.). With the pressure set at 500 pounds, the liquid maintains itself at that temperature; as this is lower by several degrees than the room temperature, heat flows in and causes the liquid to simmer quietly. About 25 per cent of the liquid boils away. The vaporized portion is sent to a special compressor which delivers it as gas to the main compressor gas line, at the pressure of 1000 pounds.

The 32° F. liquid from the evaporator is admitted to the press chambers (Fig. 80); these have movable tops and bottoms, worked by hydraulic pressure. The chamber is 20 inches by 20 inches, and 24 inches to 30 inches deep. The liquid enters through an ordinary nozzle; part of it expands to gas, and draws its heat largely from the incoming liquid which is thus solidified to a fluffy snow. The gas formed is drawn off constantly by the suction line of the main compressors and recompressed. By operating the top and bottom walls, the snow is compacted to a solid block 20 inches by 20 inches by 10 inches. Each press makes 6 to 8 cakes per hour. The density of the resulting cake is controlled by the amount of snow pressed into the 10-inch space. After discharge to a conveyor, the block reaches band saws, which cut it into four smaller blocks, each a 10-inch cube, weighing about 20 pounds. This is wrapped in brown paper and stacked

[30] The Dry Ice Corporation's plant at Niagara Falls, N. Y.

in a specially insulated railway car for transportation to distant points, or into trucks for local delivery.

Of the liquid delivered to the press, 20 to 45 per cent is solidified; the rest turns to gas and must be reliquefied. The colder the temperature of the liquid CO_2 and the colder the press chest, the higher the percentage frozen. Based on heat content, it is found that it takes 3.75 pounds of liquid to produce 1 pound of solid. The expansion in the chest is to atmospheric pressure.
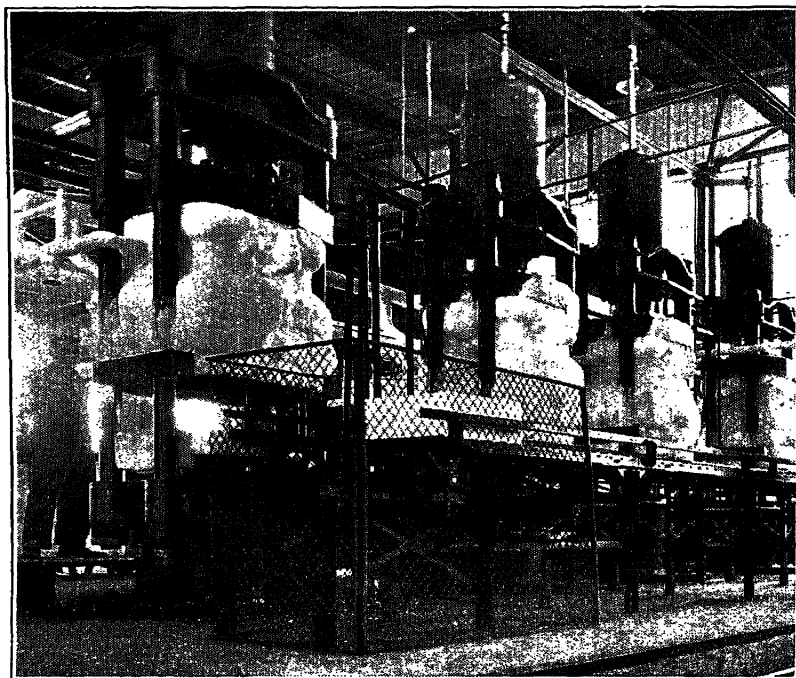
FIGURE 80.—Press chambers, in which the carbon dioxide snow is pressed into blocks; one of the blocks may be seen on the conveyor. (Courtesy of the Dry Ice Corporation of America, New York.)

The critical temperature [31] of carbon dioxide is 88° F. (31.1° C.), the critical pressure 1073 pounds. At 70° F. (21° C.), it is considerably below the critical temperature, so that a pressure of 1000 to 1100 pounds suffices to keep it in the liquid state.

It will be clear that much of the expense in the plant will be that for recirculating the carbon dioxide gasified at the presses. The compressors are four-stage machines: 0 to 5 pounds, 65 to 75 pounds, 300 to 325 pounds, and 1000 to 1100 pounds. From the last stage the gas enters oil removing filters, then a condenser cooled with tap water, which reduces its temperature to about 70° F. (21° C.). In the condenser, the carbon dioxide liquefies, and enters the "evaporator" with the new liquid, at the same temperature and pressure.

[31] The critical temperature is the temperature just above which no pressure, no matter how great, can liquefy the gas; the critical pressure is the pressure which just suffices to liquefy the gas at the critical temperature.

Carbon dioxide from any sources may be made into the solid form.

The uses of solid carbon dioxide are, at present, mainly for the preservation of foods. A railway car may be loaded with its perishable fruit, meat or vegetables, and a given number of blocks of dry ice placed on top of the goods so that the vapor will pass downward and form a heat-consuming blanket. The temperature attained is lower than with ice and salt mixtures, and may be regulated by the amount of dry ice per car. The shunting of the train to sidings for re-icing while en route becomes unnecessary; a single loading at the point of shipment suffices (for the average trip). Eighty-five per cent of the consumption is for ice cream cooling. The effective refrigeration from 1 pound of solid carbon dioxide when subliming at 0° F. (−18° C.) is 244 Btu. A temperature as low as −108.8° F. (−87.9° C.) may be reached by allowing the solid carbon dioxide to evaporate at atmospheric pressure; a lower temperature still is obtained when evaporating at reduced pressure, hence a means is provided of reaching and maintaining low temperatures without any machinery.

In order to expand, the industry needs not machinery nor complicated processes of manufacture, but new uses, either as a refrigerant, or as a source of gas.

QUICK FREEZING OF FOODS

Refrigeration has been employed in the meat industry, in cold storage houses for the preservation of butter, eggs, vegetables, fruit, and other perishable foods. A new kind of refrigeration is now applied to sea foods, particularly fish fillets, and to fresh vegetables and small fruit; they are not only cooled, but frozen. The fillets of fish, for example, are laid in their packing paper, are held between two flexible non-corroding metallic belts, and pass between sprays of brine at −45° F. (−42° C.); they leave the belt frozen, to be stored or shipped at once. If to be shipped, the fillets may be packed in corrugated fiberboard boxes which insulate sufficiently to keep the fish frozen for 4 to 5 days, and fresh, several days longer. The frozen foods may be stored at temperatures low enough to keep them in the frozen state.

There is an increasing demand for house refrigeration, to keep its air temperature at a comfortable point. This subject is connected with humidity relations, and is therefore discussed in Chapter 46.

Iceless Refrigerators. The various kinds of electric refrigerators which are displacing the ice chests are operated on the same principle as the ammonia refrigerating machine, but on a small scale. The working substance may be sulfur dioxide, methyl chloride, ammonia, a hydrocarbon, dichlor-difluoromethane, or other suitable agent; it is compressed by small motor-driven compressors. The heat of compression is removed by a current of air or by a trickle of water. The liquid so formed is then expanded, consuming heat which is drawn from the chest and its contents. The gas is then recompressed, and put through the next cycle.

Silica Gel Refrigerators. Other types absorb a vapor in silica gel,[32] or other solid absorbent, and use the heat of evaporation of the liquid for cooling. After the gel is saturated, its adsorbed mass is driven out by heat, thus revivifying the gel; in the meantime, a twin unit carries the load.

OTHER PATENTS

U. S. Patents 2,040,407 and 2,040,406, chemical heating composition, to produce heat by chemical action.

PROBLEMS

1. A swimming pool with an area of 25 feet by 70 feet contains water to an average depth of 7.13 feet. Find the cubical content and the weight of the water it contains. The water enters at a temperature of 45° F., and must be heated to 68° F. How many pounds of coal are needed to furnish that heat, if 73 per cent of the heat value in the coal reaches the water in the pool? How many gallons of fuel oil, if its specific gravity is 0.9, and the efficiency of heat transfer the same as for coal? For the same pool, at another season, the water enters at 32° F., and must be heated to 72° F. How many pounds of anthracite must be burned and used, if 73 per cent of the heat value in it reaches the water? All necessary heat values and conversion figures will be found either in this chapter or in the appendix.

2. Dry ice in Los Angeles can be made purer and just as cheaply from CO_2 from combustion of natural gas as from the gas wells developed in several places. This is due to the fact that the power which can be generated by burning natural gas under a boiler is just about sufficient to compress the CO_2 which can be recovered from the flue gas.

A dry ice plant burns natural gas (CH_4), absorbs the CO_2 formed in Na_2CO_3 solution, and recovers and compresses the pure CO_2, forming a 220-lb. cake of dry ice every 10 minutes.

(1) Assuming only 50 per cent of the CO_2 formed to be recovered, what volume (cu. ft.) of CH_4 is burned per hour? (60° F., atm. press.)

(2) Assuming weights of 90 lb./cu. ft. for dry ice and 57 lb./cu. ft. for water ice, and refrigerating effects of 275 Btu. and 155 Btu. respectively, what weight of dry ice is equivalent to a ton of water ice, and what volume (cu. ft.) will each occupy?

(3) If dry ice costs $0.02/lb., what is the equivalent value of the water ice?

(4) If the soda liquor starts at 9.0 lb. Na_2CO_3/cu. ft. and 60 per cent is carbonated to $NaHCO_3$ and 20 per cent remains as $NaHCO_3$ at the discharge from the evaporator, how many cu. ft. of liquor (neglecting volume changes) must be carbonated per minute to handle the above production?

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[32] *Ice and Refrigeration*, **74**, 217 (1928); **78**, 331 (1930).

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The inhabitants of a city must have a plentiful supply of water, for drinking, cooking, washing, and sanitary purposes. It is one of the few public services to which the American can point with pride. The largest city in the country brings its water 92 miles, water which is palatable and safe at all periods of the year. A second problem which the congregation of so many people in cities has raised is that of sewage disposal; in its solution, it is gratifying to contemplate that an American chemist, Dr. H. W. Clark of the Massachusetts Board of Health, has played a major rôle by his discovery of the principles of the activated sludge process.

Chapter 13 [1]

Water for Municipalities and for Industrial Purposes. Sewage Disposal Plants

In every city, a supply of water is provided for domestic, public, and industrial uses. The chemical industries at times require water which meets certain specific requirements; in some cases it must be free from even traces of heavy metals; in others, its purity is of no moment, but it must be cold the year around. The industries situated within reach of the city water draw their supply, or at least part of it, from the city main. For that reason, water for municipal purposes will be considered first, and the additional demands made by the industries, after that.

WATER FOR MUNICIPAL PURPOSES

A water for municipal purposes, for drinking, for general domestic and industrial consumption must be (1) hygienically safe, (2) reasonably soft, (3) practically colorless, and (4) free from objectionable odor and taste.

Absolutely pure water, consisting only of H_2O and its polymers $(H_2O)_x$ is a laboratory curiosity, and most difficult of preparation; such a water would be soft, colorless, odorless, and would have a p_H value of 7. It is this latter requirement which is difficult to meet, for traces of carbon dioxide lower it. Rain water collected in a cistern would be soft; it is still the custom in the country to build such cisterns in order to have water which soaps easily for the washing. River and lake waters are surface waters; they are comparatively soft (that is, low in mineral content), and are most likely to contain easily soluble salts and sediments. Ground waters, from artesian wells for example, are usually free from suspended matter, but are much harder (that is, richer in calcium and magnesium salts) than surface waters in the same vicinity. In regions of heavy rainfall, the surface waters contain less mineral matter, because of dilution. Sea water is not water at all, in comparison to the waters discussed just now, but a salt solution. It contains 3.5 per cent salts, of which 80 per

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cent are common salt, NaCl. This is an enormous concentration, yet it must be added that, nevertheless, sea water is used industrially; for example, for the cooling of turbine steam condensers, in plants located at the sea shore. In surface waters and ground waters, the amount of impurities is so small that it is expressed not in per cents, but in parts per million (ppm.), as for example, 300 ppm., which means 300 grams dissolved matter in 1 million grams of water. Roughly, sea water is 100 times more concentrated.

In speaking of soft waters and hard waters, it is well to classify more closely, and in figures:

> Soft water contains less than 100 ppm. total solids.
> Medium hard water contains from 100 to 200 ppm. total solids.
> Hard waters contain from 200 to 500 ppm. total solids.
> Saline water contains 500 ppm. and over total solids.

"Parts per million total solids" means the residue on evaporating the water on the steam bath. The classification just given is a quantitative one; but to most chemists, hardness does not mean merely a comparatively larger amount of total solids, but the presence of salts of calcium and magnesium which, with a soap solution, do not allow foam formation until they are precipitated as insoluble soaps. In general it so hap-
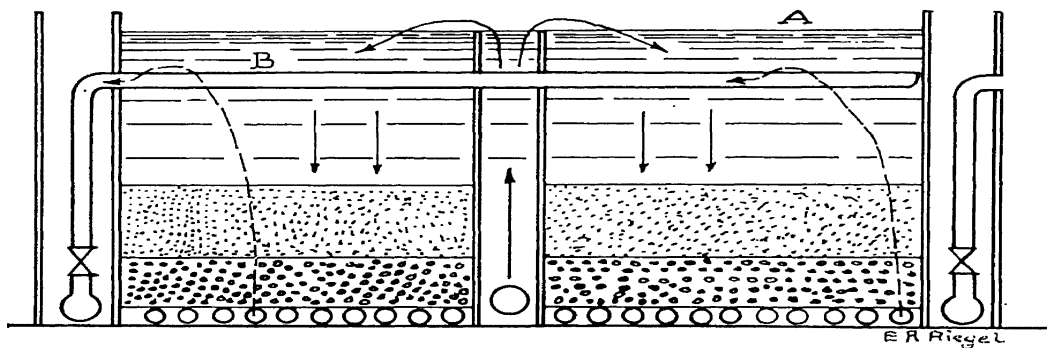
FIGURE 81.—Sand filter, to show method of washing. The water to be filtered enters as shown by full arrows, and passes through sand, gravel, and under-drains to clear wells (not shown); this water reaches level *A*. To wash, the flow is reversed; water enters through the underdrains, rises through gravel and sand, and leaves through gutter *B*. At such times, the level of the water stands at *B*.

pens that the residual solids for medium and hard waters are over half calcium and magnesium compounds, so that the figures reflect the amount of these salts as well as the total for all salts. With saline waters, it is different; here the total solids are likely to be mainly sodium chloride.

The methods practiced for the purification of water for municipal purposes will be shown by means of several examples.

Buffalo Municipal Water Filtration Plant. For Buffalo, water is drawn from Lake Erie, at a point at the head of the Niagara River. The water enters a tunnel one mile long, 12 feet by $11\frac{1}{2}$ feet in cross-section, through 12 ports, each 6 feet square, opening 20 feet below the surface of the lake. The tunnel runs into a canal which feeds the "low lift" centrifugal motor-driven pumps which deliver the raw water to the coagulating basin against a head of 17 feet, through the raw water discharge conduit. In this conduit, twin venturi tubes, 70 inches by 48 inches, meter the water. "Filter alum" is added at this point, at the rate of 50 pounds to 1 million gallons. The water is distinctly alkaline, so that aluminum hydroxide, the alum floc, forms without other addition. The water moves slowly through the coagulating basin, taking a zigzag course set by baffle plates. The basin is 300 feet long, 100 feet wide, and 25 feet deep. After 3 hours, the water leaves it and passes to the sand filters.

There are 40 filters, each 53 feet by 33 feet in area. Perforated underdrain pipes are covered by 16 inches of gravel made up of five graded layers, and overlaid by 26 inches of sand (grain size 0.38 to 0.45 mm.). The filter capacity is 2 gallons per square foot per minute, 4 million gallons per day for the filter, and 160 million gallons per day for the plant. The filter capacity sets the capacity for the station; the low-lift pumps have a 50 per cent excess capacity, the tunnel a 180 per cent excess capacity. The filtered water passes to clear wells, and flows through a canal to the pumping station. The chlorine is injected in the canal, at the rate of 2 pounds per million gallons.

The reaction between the "filter alum" $Al_2(SO_4)_3 . 18H_2O$ and the alkalinity in the water, in the form of calcium bicarbonate, is:

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 = 2Al(HCO_3)_3 + 3CaSO_4$$
$$Al(HCO_3)_3 = Al(OH)_3 + 3CO_2$$
$$alum \; floc$$
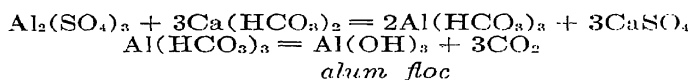
The alum floc is voluminous; as it slowly settles, it carries with it most of the suspended matter, and a part of the bacteria (the count is reduced by about half). The choice of the coagulant is a particularly happy one in another respect. A part of it is in the colloidal state, with a positive charge in the colloidal sense, so that it is most efficient in precipitating the naturally occurring colloidal materials in the water, which are almost exclusively negative.[2]

In the clear water conduit a venturi meter 12 feet by 6 feet records the volume of flow. The station is amply provided with level gages, meters, and pressure recorders; every filter has a set.

About 15 per cent of the suspended matter, including the alum floc, settles out in the coagulating basin; the rest is caught by the filter. After 15 hours, the filters are rid of their dirt by reversing the flow of the water, so that it rises through the sand and empties into gutters

[2] The precipitation of a negatively charged colloidal suspension by a positively charged colloidal suspension is called mutual precipitation. The positive colloidal particle is $[Al(OH_3)]nAl^{+++}$. For a closer study, *see* the chapter "Chemistry of Coagulation," in "Chemistry of water and sewage treatment," by A. M. Buswell, New York, Chemical Catalog Co., Inc., 1928.

which, while the filter is working normally, are submerged. The washing requires 10 minutes. The coagulating basin is divided into two independent halves, so that it can be cleaned without interruption of the

TABLE 22.—*Analyses of Birmingham, Ala., Water.*

	May, 1932	October, 1931
Total solids	140 ppm.	124 ppm.
Total hardness, as $CaCO_3$	67	107
Iron Fe	0.07	0.01
Calcium Ca	17	33
Magnesium Mg	5.9	6
Sodium Na	19	4.1
Potassium K	1.3	1.2
Carbonate CO_3	0	0
Bicarbonate HCO_3	54	120
Sulfate SO_4	61	15
Chloride Cl	2.0	2.0
Nitrate NO_3	0.45	0.40
Silica SiO_2	7.80	5.80

service; this is done twice a year. One and one-half per cent of the filtered water is consumed in the washing of the filter beds.

Municipal Plant at Birmingham (Alabama). At the Birmingham station, an unusual impurity is removed and made to share in the work of purification; this impurity is manganese. During the late autumn, when the level of the supply reservoir (Lake Purdy) has been lowered considerably, the content of manganese in the water rises abruptly. The

TABLE 23.—*Analysis of a Composite of Weekly Samples Over July, August and September, 1936, Taken at the Head of the Colorado River Aqueduct, 150 Miles Below Boulder Canyon Dam.*

Calcium (Ca)	58 ppm.
Magnesum (Mg)	18
Sodium (Na)	52
Bicarbonate (HCO_3)	134
Chloride (Cl)	41
Sulphate (SO_4)	156
Boron (B)	0.15
Fluorine (F)	0.3
Total dissolved solids	415
Total hardness as $CaCO_3$	219
Carbonate hardness as $CaCO_3$	110
Noncarbonate hardness as $CaCO_3$	109

For 1936, the average (unweighted) hardness of the raw water at the Boulder City treatment plant was 280 ppm. Softening of the Colorado Aqueduct water to a total hardness of not over 125 ppm. has been recommended. This would then be the water distributed to Los Angeles, with chlorination with the present equipment. [Courtesy of the Metropolitan Water District of Southern California, F. E. Weymouth, General Manager, Los Angeles, California.]

raw water, before being treated with a coagulant, which is aluminum sulfate in this case, is treated with sufficient chlorine to convert all the manganese present into the chloride; this is hydrolyzed by the alkalinity of the water, and forms a flocculent precipitate. This precipitate assists in the clarifying action of the aluminum hydroxide, and in this way this

undesirable impurity is removed, and at the same time functions as coagulant, allowing the corresponding amount of aluminum sulfate to be saved.

During the greater part of the year, the "filter alum" added is 0.7 to 0.8 grain per gallon of water; a small amount of lime is introduced when necessary, to keep the p_H value near 6.9. Table 22 gives typical analyses.

Other Plants. At Marseilles, France, an apparatus for the sterilization of the city water by means of ultra-violet rays (instead of chlorine) has been in operation for several years and has proven highly satisfactory. A primary requisite for such treatment is a source of cheap electric power.

New Orleans (Louisiana) takes its water from the Mississippi; the period for coagulation is 24 hours because of the very fine sediment in the water. The usual period varies from 2 to 6 hours.

In the adjoined table, information on the Colorado river water, as it will be delivered to Los Angeles in the near future, is presented.

For New York City,[3] just under 1 billion gallons per day is supplied from four different sources; surface water from the Catskill system (Ashokan and other basins), the Croton system, and the Long Island system; a comparatively small portion (50 mgd.) comes from wells. The main single source is the Ashokan system; a tunnel brings it from the west side of the Hudson, under the river, to the Kensico reservoir, and from there south through Westchester County to the city line, a distance of 92 miles.

Sufficient chlorine is injected, at a number of points (50), to produce a constant residual chlorine varying from 0.05 ppm. in water going directly into the distribution system, to 0.10 ppm at the more distant stations. The actual dosage varies from $\frac{1}{2}$ pound to 5 pounds per million gallons.

In order to control a colloidal clay turbidity occurring at intervals in the Catskill system, the water is treated in the aqueduct between Ashokan and the Kensico reservoir with soda ash and filter alum: soda ash from 0.25 to 0.50 grain per gallon, alum from 0.50 to 1.0 grain per gallon, according to the turbidity which varies from 10 ppm to 100 ppm. The alum floc and turbidity is settled out in the Kensico reservoir. An efficiency of 95 per cent removal of turbidity has been attained.

The Catskill water is aërated at both Ashokan and Kensico by projecting it vertically upward into the air through about 1600 nozzles. The necessary head is furnished by gravity.

Copper sulfate, an algicide, is applied at the Ashokan basin by dragging crystals in burlap bags suspended from a rowboat or motor launch, traveling over the surface back and forth.[4] It is also applied by dry feed at various points, while at Muscoot Dam, Croton Lake, it is fed in continuously (for the last two years) by pumping a dilute solution through a 1000 foot pipe with nozzles every two feet, and about one foot under the surface. In 1931, about 100 tons in all were used.

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[3] From data kindly supplied by the Bureau of Water Supply, New York City.

[4] "Control of miscroscopic organisms in public water supplies, with particular reference to New York City," Frank E. Hale, *J. New England Water Works Assoc.*, **44**, 361 (1930).

The water is distributed to the five boroughs by a circular tunnel cut in the rock below, measuring 15 feet in diameter at the northern
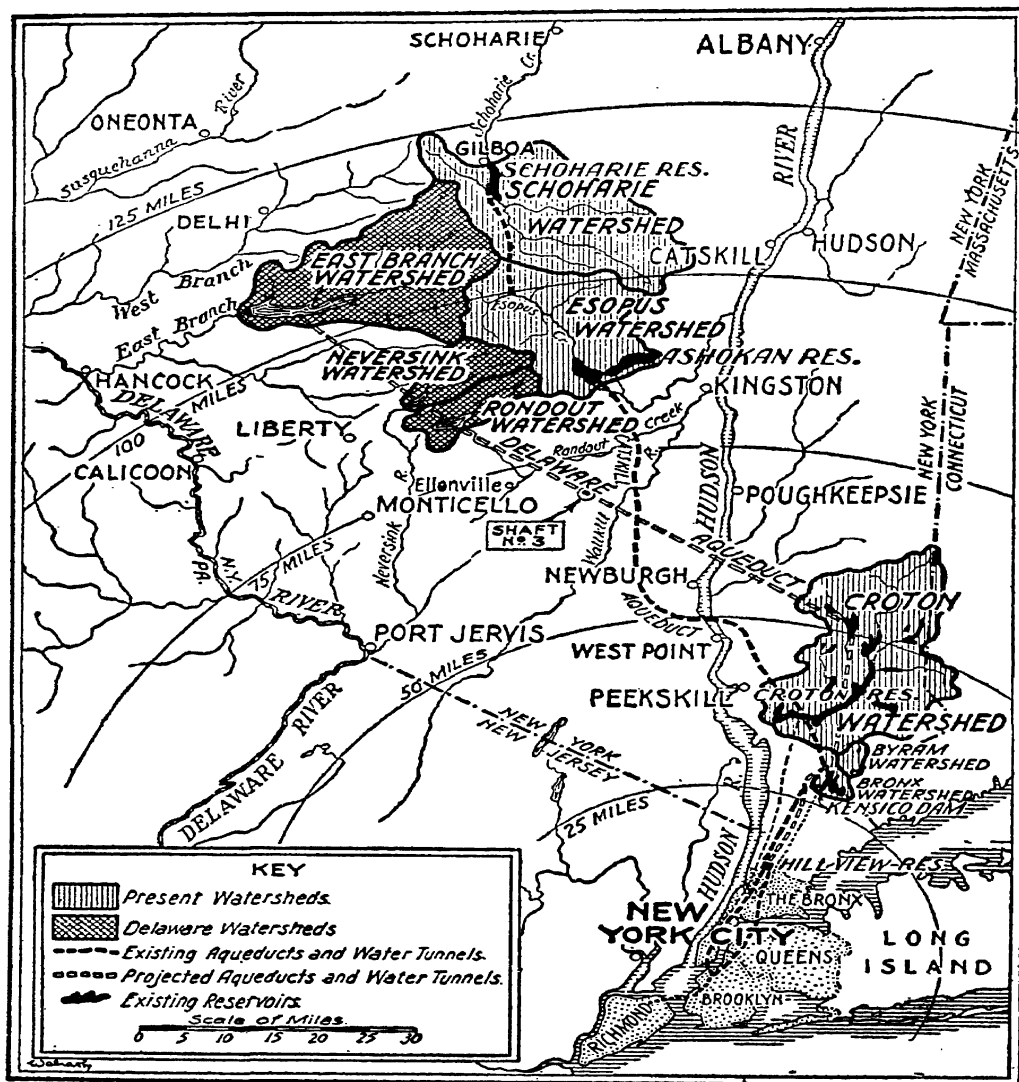
FIGURE 81a.—The sources of supply of potable water for the City of New York (as planned in 1937). [By permission.]

end and 11 feet near the end of the system. The tunnel lies 200 to 750 feet below the street.

Average analyses of the water supply from the various sources are given in Table 24.

TABLE 24.—*Average analyses of Catskill, Croton, and Long Island Water Supplies for the City of New York, for the Year 1936.*

	Catskill	Croton	Long Island
Turbidity (ppm. silica)	2	1	2
Color (ppm. platinum)	5	9	5
Odor	1v	1v	1v
Albuminoid ammonia (ppm. nitrogen)	.056	.088	.053
Free ammonia (ppm. nitrogen)	.028	.026	.084
Nitrite (ppm. nitrogen)	.001	.001	.002
Nitrate (ppm. nitrogen)	.12	.20	2.04
Total solids (ppm.)	44	71	167
Fixed solids (ppm.)	31	51	117
Chlorine in chlorides (ppm.)	1.8	3.2	30.1
Hardness (ppm. calcium carbonate)	22	40	64
Alkalinity (ppm. calcium carbonate)	11	30	19
Iron (ppm.)	.17	.28	.55
Hydrogen ion (p_H)	6.8	7.05	6.5
Bacterial count, per cc. (37° C. Agar)	3	21	7
*B. coli per 10 cc.	.008	.05	.0007
Microscopical: total organisms, s t a n d a r d units per cc.	115	185	10
Amorphous matter, st. u. per cc.	505	970	725

(Source of samples: Catskill, shaft No. 23, Brooklyn; Croton, 9th avenue and 18th street, Manhattan; Long Island, Ridgewood pumping station, Brooklyn). (By courtesy of Department of Water Supply, Gas and Electricity, Patrick Quilty, Acting Chief Engineer, and Frank E. Hale, Director of Laboratories, City of New York.)

* All municipal water analyses record *Bacterium coli* separately and in addition to the complete bacterial count, because it is the tell tale for the presence of animal or human waste in the water.

General Remarks on Water Purification. For municipal purposes, the factor of safety to health is the controlling one, so that the purification is really a sterilization, a destruction of bacterial life, with other improvements in taste and color incidental. The question of hardness does not matter very much. For sterilization, chlorine gas is almost universally used, but other agents are: bleach, ammonia gas and chlorine gas combined; ultra-violet rays from mercury arc lamps, quartz enclosed. If turbidity is present, it may be removed by the action of a coagulant; a high proportion of bacteria is removed, incidental to this clarification. This operation precedes chlorination.

When a coagulant is needed, for the removal of turbidity and suspended matter, aluminum sulfate is almost the universal choice; it is called "filter alum." The amount of filter alum required depends upon the turbidity, and to a considerable degree upon the temperature of the water, the colder water requiring more.[5]

Salts of the alkali metals and alkaline earths are present in most waters; the most common are calcium, magnesium, sodium and potassium, combined with the bicarbonate, carbonate, sulfate, chloride, nitrate, and nitrite ions. The alkalinity is usually sufficient to precipitate aluminum hydroxide from added alum, but if it is not, an appropriate amount of milk of lime or soda ash is added.

[5] *See* curves showing relation between amounts of coagulant, temperature of water, and turbidity of coagulated and raw water, "Water Purification," Joseph W. Ellms, New York, McGraw-Hill Book Co., 1928. 2d ed., p. 412.

The presence of 0.1 to 0.2 ppm. of iron is enough to be troublesome, especially in the staining of fabrics and plumbing fixtures. It also stimulates the growth of *Crenothrix,* a thread-like organism which decomposes iron and manganese compounds with the formation of their hydroxides, and gives the water a bad taste and odor. When iron is present, it is generally in the form of ferrous carbonate or bicarbonate. On exposure to the air these compounds oxidize, and insoluble ferric hydroxide is formed. As small a quantity of iron as 2 ppm forms a bulky and unsightly precipitate, sufficient to plug pipes. Iron may be removed by aëration followed by sedimentation. Aëration is accomplished by spraying the water into the air, or causing it to cascade over a bed of coarse material. Other aims in aëration: obnoxious gases are able to escape, certain small organisms are destroyed, and taste improved. Algae frequently give rise to the formation of a green scum in reservoirs and water mains which must be removed mechanically, or better, prevented from forming by a chemical agent. Of the many algicides recommended, copper sulfate is the cheapest and most efficient.

The removal of phenol from gas and coke plant wastes which might reach the municipal supply is described in Chapter 14.

The Use of Ammonia in Water Purification

In a few localities since 1918, in a fast growing number since 1930, ammonia is injected into municipal water supplies in addition to chlorine or bleach. This use of ammonia serves to lower the amount of chlorine (or bleach) needed for bacteria removal; it decreases the taste due to chlorinated phenolic bodies, and successfully prevents slime formation in mill waters and power plant condensers. It was pointed out by Rideal (in 1910) that a hypochlorite solution containing 1 per cent available chlorine had a phenol number of 2.18, while the same solution mixed with one equivalent of ammonia had the coefficient 6.36, more than three times greater. The chlorine and ammonia form chiefly monochloramine, NH_2Cl, a powerful bactericide, yet a substance less energetic chemically than chlorine, so that it does not attack such organic molecules as phenol. The ratio of ammonia to chlorine should be as 1 is to 4; when necessary, as 2 is to 3. The reaction is: $2NH_3 + Cl_2 = NH_2Cl$ chloramine $+ NH_4Cl$.

A striking success was scored by the combined ammonia and chlorine system at the Tampa (Florida) water works. The average dose before the adoption of the new system was 16 pounds of chlorine per million gallons. This left a chlorine residual amount of 0.25 ppm. In the new system, 5.6 pounds per million gallons of chlorine, and 1.9 pounds of ammonia for the same volume were used. This left an average residual of 0.35 ppm., higher than previously, and enough to eliminate aftergrowth altogether. The cost is $0.94 against $1.54 by chlorine alone. A swampy odor and taste have been eliminated.

The water in swimming pools is sterilized by passing it over a quartz mercury arc lamp, whose short rays (ultra-violet) are effective in reduc-

ing the bacterial count. The combined ammonia-chlorine purification has been applied in a number of swimming pools,[6] with satisfactory results. The method most in use, however, is the application of chlorine.

WATER FOR INDUSTRIAL PURPOSES

In the further consideration of the supply of water for the industries, a number of requirements must be met. The most important is that the water should be cheap.

Over half the water used in chemical plants is for cooling; it would be economically impossible to purchase city water, assuming that the capacity of the city system would be adequate. The composition for cooling water is of no great importance; its function is to carry away heat, by warming of the liquid water, or by evaporation. Water fed to steel jackets forming the walls of a copper blast furnace; water flowing around a Cellarius vessel through which hydrogen chloride passes, and cooling water flowing through the jacket of a three-stage compressor, illustrate the first; a trickle of water over an ammonia condenser, the second.

The water is drawn from a near-by river or lake, passed through a pressure type sand filter, in order to remove any suspended matter which might clog pipes and valves. A fish trap protects the pump, which may be a Connersville blower, or a centrifugal pump. The sand filter is similar in construction and operation to the gravity type described, except that it is contained in a cylindrical steel shell, either horizontal or vertical. The water enters at the top and leaves at the bottom, through a riser which brings the water to an elevated tank, from which it is fed to the parts to be cooled, by gravity. The capacity of the pressure sand filters vary with the size, from 500 to 36,000 gallons per hour.

If available river water is not cool enough, artesian wells are driven; these frequently have maintained a flow of water of 54° F. (12.2° C.) the year around.

Filtering may be dispensed with, if the piping is short and accessible; brackishness does not matter if the vessels to be cooled are stoneware. In the case of cast iron and steel, an occasional replacement because of corrosion by the cooling water is preferable to an elaborate installation for treating it.

Another considerable volume of water is used in the chemical plants for solution and dilution; as a rule, a reasonably pure river water is all that is needed.

These water requirements are usually readily met, because the chemical plants are purposely located near an abundant supply of water, to be had for the pumping costs.

Water Softening. In dye application plants, in laundries, in rayon plants, and others, the water used in processing must meet narrower

[6] "Precautions needed in the ammonio-chlorine treatment of swimming pools," Lyle L. Jenne and Henry R. Welsford, *Ind. Eng. Chem.*, **23**, 32 (1931).

requirements. As a rule, it must be soft. If the only available supply of water is hard, the water must be treated, in order to remove dissolved calcium and magnesium salts. This is done by means of (1) lime and soda ash addition, followed by settling and filtering, or (2) trisodium phosphate addition, or (3) contact with zeolites. The softening of water for use in steam boilers has been discussed in the preceding chapter; some supplementary remarks will be given here.

(1) The reason for combining the lime with the soda ash treatment is as follows: The carbonate hardness (old temporary hardness) leads to the reactions: $Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$, and $Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2H_2O$. The magnesium carbonate is fairly soluble (100 ppm.) and requires an excess of lime: $MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3$. The magnesium hydroxide is insoluble, as is the calcium carbonate, and both settle out. If magnesium chloride is present, the reaction $MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2$ takes place, and although magnesium hydroxide precipitates, an equivalent amount of calcium chloride is in solution; no true softening has been achieved. Accordingly, sufficient soda ash is added to precipitate the calcium chloride, as well as any calcium chloride, nitrate, or sulfate originally present, which remain unattacked by lime: $CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$, or $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$. All the dissolved salts mentioned in this paragraph except the bicarbonates make up the non-carbonate hardness; only the calcium sulfate is scale-forming, but any of the others will bind soap or dyes. It should be understood that the magnesium sulfate undergoes the same reactions as the chloride.[7]

It is clear that the amount of lime and soda ash will be determined by the analysis of the water, supplemented by the actual results of the treatment. A large installation for softening would resemble a municipal filtration plant. On a smaller scale, two tanks may be used; in one, the raw water receives the dosage of chemicals, and after stirring, is left to settle; in the meantime, the other may be drawn off, the comparatively clear water only passing to the sand filter, while the main part of the precipitate is run to the sewer. Hot water is frequently employed; the treatment and settling take place in a large tank; here again, the clear supernatant water only passes to the filter. With the hot water, the action and the settling of the precipitate are more rapid. In an hour, an effluent with only 25 ppm. is obtained. The application of trisodium phosphate, (2), an alkaline substance, is similar.

(3) In contact with zeolites,[8] the following reaction takes place:

$$Na_2Ze + Ca(HCO_3)_2 = CaZe + 2NaHCO_3$$
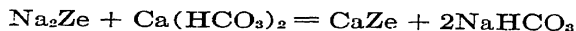
The symbol Ze stands for the zeolite radical: $2SiO_2.Al_2O_3.Na_2O$, which is now written Na_2Ze. This is preferable, because a zeolite containing 2 molecules of SiO_2 is not suitable, and must be replaced in

[7] For a more detailed treatment, *see* the chapter on "Lime and soda process" in "The chemistry of water and sewage treatment," A. M. Buswell. New York, Chemical Catalog Co., Inc., 1928.
[8] For the manufacture of these, *see* U. S. Patents 1,343,927 and 1,304,200.

practice with zeolites containing from 5 to 13 molecules of SiO_2. The water gives up its calcium and receives an equivalent amount of sodium. After 6 to 8 hours, the flow of raw water is stopped, and the container filled with brine (saturated sodium chloride solution). (See Fig. 82.) The reaction

$$CaZe + 2NaCl = Na_2Ze + CaCl_2$$
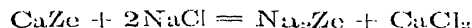
takes place, in a period which was originally 6 hours. After that time, the salt solution is drawn off, the vessel rinsed, and the raw water may be sent in. The "hardness" in the form of calcium and magnesium
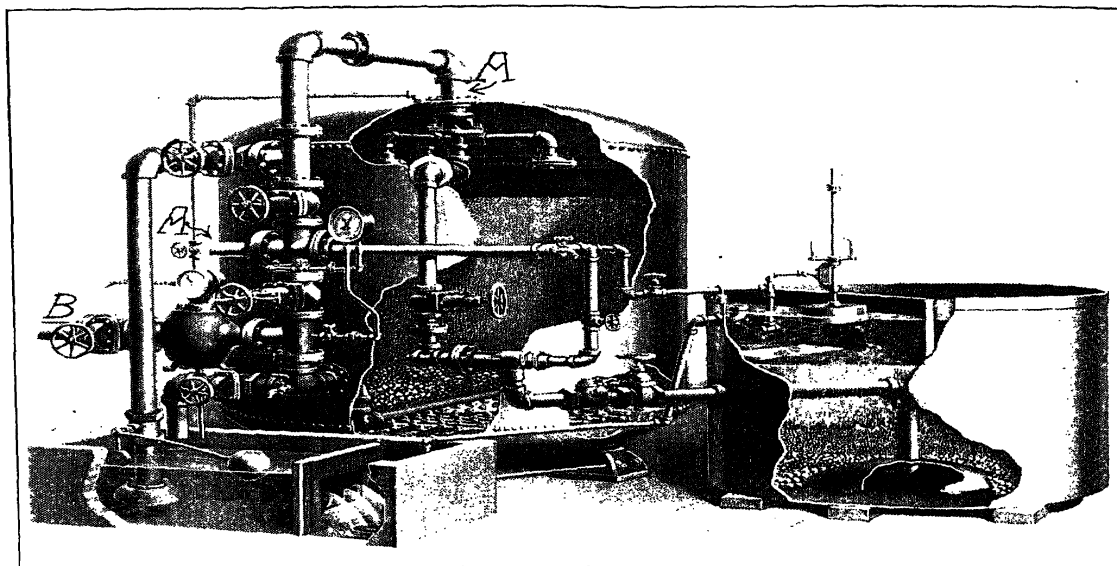
FIGURE 82.—Permutit vertical zeolite water softener, pressure, downflow type, showing the zeolite bed in the softener. Raw water inlet *A*, treated water outlet *B*, brine tank with bed of salt, and brine pipe with ejector from bottom of brine tank to the distributors at top of zeolite tank. (Courtesy of The Permutit Co., New York.)

chlorides passes out with the salt solution. Improvements in the manufacture of zeolite have led to the rapid type of exchange material, the gel type or porous type; the softening action is more rapid, and the regeneration also (30 minutes). A successful commercial zeolite is made from New Jersey green sand (glauconite), by special treatment. The apparatus for softening resembles the pressure sand filters, with zeolite in grain form instead of the sand. It has been found that upflow as well as downflow may be practiced; with upflow a greater softening capacity is reached.[9]

The softening capacity for a slow or non-porous zeolite is 2500 grams

[9] "Recent developments in zeolite softening," A. S. Behrman, *Ind. Eng. Chem.*, **19**, 445 (1927). "Zeolites, mining, processing, manufacture, and uses," Eskel Nordell, 9th annual Michigan Conference on water purification, Bull 61, Jan., 1935.

(as $CaCO_3$) per cubic foot of zeolite mass (100 pounds per cubic foot); for the porous type, up to 10,000 grains per cubic foot of zeolite mass (60 pounds per cubic foot). The effluent may be as low as 5 ppm. in hardness.

A plant which draws its own water from a river would send a portion of it through the zeolite softeners or lime-soda ash system, for use in its boilers, or in the washing, dissolving or diluting operations which call for soft water. The greater part of the water supply would serve untreated.

Among the new zeolite developments should be mentioned Zeo-Karb, which can be used either on the sodium cycle or the hydrogen cycle.

The soluble salts of sodium and potassium in the raw water are not removed; in fact, additional soluble salts of sodium are introduced by the softening reactions. A very hard water (say 400 ppm.) for a municipality sent through a zeolite plant, for example, would contain enough salt to give a strong taste, which the consumers would probably dislike more than the original, tasteless hardness.

It might be well to enumerate the requisites for waters to be used in certain important industries. Boiler water should be as soft as possible to prevent incrustations on boiler plates and tubes. Water to be used in laundries should be relatively soft and free from iron and manganese. Paper mills require that a water should not contain iron, since this stains the paper, and an excess of calcium and magnesium is to be avoided because they tend to precipitate the rosin soaps which are used in sizing the paper. Water containing sulfates, alkali carbonates, nitrates, and bacteria must be avoided in sugar refineries if the sugar is to crystallize well, is not to be deliquescent, and not decomposed while standing in storage. Alcohol distilleries require a cool water containing few micro-organisms and relatively little sodium and magnesium chlorides. Bakeries require a potable water with a minimum of organic matter which might affect the action of yeast. Water to be used in dyeing should be free of iron, and contain little hardness in order to avoid the formation of insoluble lakes, which give impure shades and often spot the fabric. Wool and cotton mills require a very soft water in order that undue amounts of soap will not be wasted in the washing of the yarn. Viscose silk plants must have water absolutely free from copper. The soft beverage trade usually uses distilled water.

"Heavy water", that is water containing the heavy hydrogen isotope deuterium (mass 2) instead of hydrogen (mass 1), plays no rôle as yet in the industrial world.

Sewage Disposal Plants

Methods for sewage disposal may be grouped into two classes, those without treatment, and those with treatment of the sewage. By sewage is meant any waste at all which is sent out of households and habitations of any kind, manufacturing plants, and city streets. Its composition varies according to origin, and in some cases special treatment may be

required; the present discussion will be limited to the more typical city wastes, in which putrefiable organic matter is carried away by a considerable amount of flushing water.

Of the methods in the first class, the disposal by discharge into a water course is an example, and is a case of disposal by dilution. It is extremely simple, and besides some screens to catch large and coarse objects, the apparatus is of no importance. If the flow of the water course is 7000 gallons per capita per day, disposal by dilution is acceptable.

In the second class, a distinction may be made between settling methods, and complete digestion followed by settling and filtration.

Settling Methods. The raw sewage is admitted to a sedimentation tank, in which the mud settles. The effluent is discharged into rivers or first filtered, then discharged, while the sediment passes to another tank where it is digested or rotted. After a period, it is pumped in slurry form to filter beds, which allow the water to flow off, while the now inoffensive mud remains behind. During the rotting period, micro-organisms grow, with the simultaneous evolution of gases, mainly methane and carbon dioxide. In some of the European installations, the gas is burned under a boiler.[10]

Imhoff Tank. Simplicity in construction and operation is secured by placing the sedimentation tank above the digestion tank, so that the sediment may be fed to the digestion tank by gravity. This is the principle of the well-known and popular Imhoff tank, illustrated in Figure 83. The retention time is about 2 hours.

The effluent from the Imhoff tank is chlorinated, and then sent to the river or stream. If there is situated down river another community which draws water from the river for municipal use, the up-river plant is required to send its effluent through trickle filters, in which it is sprayed into the atmosphere, falling on a gravel and sand filter, then only, after chlorination, reaching the river.

The Imhoff tank is well adapted to small and medium size cities. It removes from 50 to 80 per cent of the total solids in the raw sewage.

Septic Tank. In the septic tank, the sediment is allowed to remain until it is rather well digested; it is really a sedimentation and digestion tank in one, and is cleaned only once a year. It has been adapted to fair-sized cities, and is in general use for single dwellings without sewer connections.

The Imhoff tank may be considered a perfected septic tank, in which the anaërobic fermentation takes place undisturbed by the flow of the sewage proper.

The sewage disposal plant for the city of *Worcester, Massachusetts* (200,000 inhabitants), is an installation of Imhoff tanks on a grand scale. The plant is in sight of U. S. Highway No. 20. The functioning of the tanks is essentially like that of the smaller plant described. The raw

[10] "Taschenbuch der Stadt-Entwässerung," K. Imhoff, Munich and Berlin, R. Oldenburg, 1932, p. 93.

sewage passes through the following divisions: grit chambers (2), screens (2), Imhoff tanks (12) and as to these, each one is 32 feet deep, and 50 by 50 feet in area, divided into 4 parts; the direction of flow is reversed once a month; dosing tanks (8), for the distribution of the partially clarified sewage upon the trickling filters; trickling filters (4), on a lower level, and

FIGURE 83.—Imhoff tank. Upper drawing, plan view of the tank, showing circulation. The flow through the tank is reversed periodically; direct flow is through gates 1, 4, 3, 7, and 9, with the others closed (solid arrows); reversed flow through 2, 8, to the tank, out through 4, 5, and 6, with the remainder closed (dotted arrows). Lower drawing, cross section; B, discharge for the sludge.
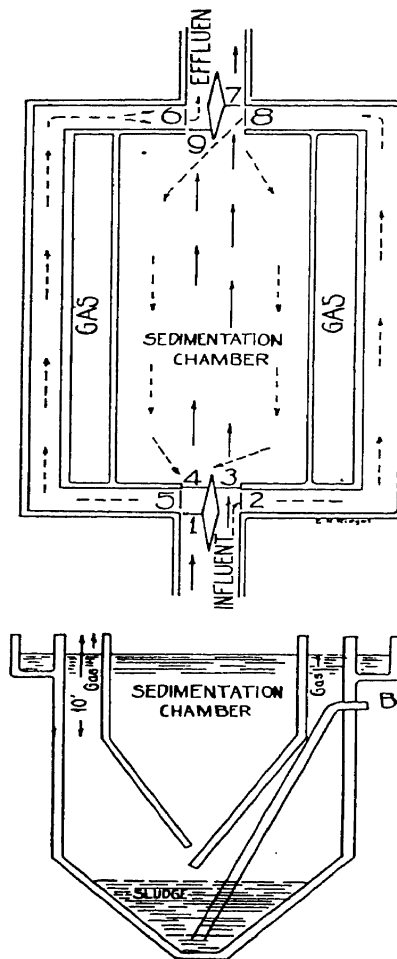
covering 13.68 acres; final settling tanks (4), to remove suspended matters from the effluent coming from the trickling filters. No chlorination is necessary; the effluent discharged into the Blackstone river may be kept indefinitely in a closed bottle at room temperature without developing any disagreeable or offensive odor. The quantity of sewage normally handled is between 17 and 24 mgd. The Imhoff tanks remove 56 to 62 per cent of the total solids. The appearance of the plant is that of a city park

Power from the sewage gas.   Reference has been made to European installations for producing power from the Imhoff tank gas.   There is now an installation in America, in Durham, N. C., in which sewage gas from activated sludge tanks, in this case, becomes the fuel for gas engines which supply all the power required by the plant.   Sludge from the primary settling basin, and skimmings from that same basin, are conditioned, by addition of lime generally, and the p_H adjusted to 7.2.   Pumped to closed digesters, this conditioned sludge, with the proper content of activated sludge, is digested at 82° F. (27.78° C.) for 30 days; the gas evolved during the digestion is discharged into a gas holder which exerts a pressure on the gas of 6 inches of water.   The gas consists of methane and carbon dioxide, and its average Btu. over the year was 723 per cubic foot. The volume over the year (1935-1936) was 16 million cubic feet.[10a]

Activated Sludge Process.   The activated sludge process "consists of the aëration of sewage in the presence of nitrifying and other organisms attached to the circulating sludge.   It rests upon observations made in the course of a study of the effect upon fish life of water polluted to different degrees by sewage and other substances." [11]

The process will be best explained in terms of an actual plant.

THE MILWAUKEE PLANT

The activated sludge process differs from the Imhoff tank and similar procedures in that it employs microbial growth under aërobic condition. Air is supplied, and the material is exposed to the open air in large rather shallow tanks through which it travels slowly.   Whatever action takes place in the digestion tanks of the Imhoff system is anaërobic (that is,

Simple Flow Sheet for the Activated Sludge Process of Sewage Disposal.

Raw sewage   grit chambers   →   screens
                                                                    ↓
                                                         25% activated sludge
                                                              addition,
                                                                    |

                                              ↓
                              aërating tanks, receive air

CO_2+CH_4 clear effluent,   readily   settled   mud,
form a   the outfall   the   activated   sludge
foam   ↓ |
and   discharged into   ↓   —
escape   lake or   in part   Dorr classifiers
                                            retained   ↓
                                            and mixed   Oliver filters
                                            with raw   ↓
                                            sewage   driers
                                            for   ↓
                                            inoculation   storage

[10a] "Sewage gas engines supply power for disposal plant at Durham, N. C.," Milton F. Merl, *Southern Power Journal*, 54, No. 12, 50 (1936).

[11] From a private communication from Dr. H. W. Clark, Chief Chemist, Mass. Dept. Public Health, to whom the observations are due.

without oxygen). Another difference is that the digestion is made complete in the activated sludge process, while the rotting in the Imhoff system is partial.

A description of the Milwaukee disposal plant will permit the tracing of the sewage through the plant. (*See* Flow-Sheet, Page 242.) The raw
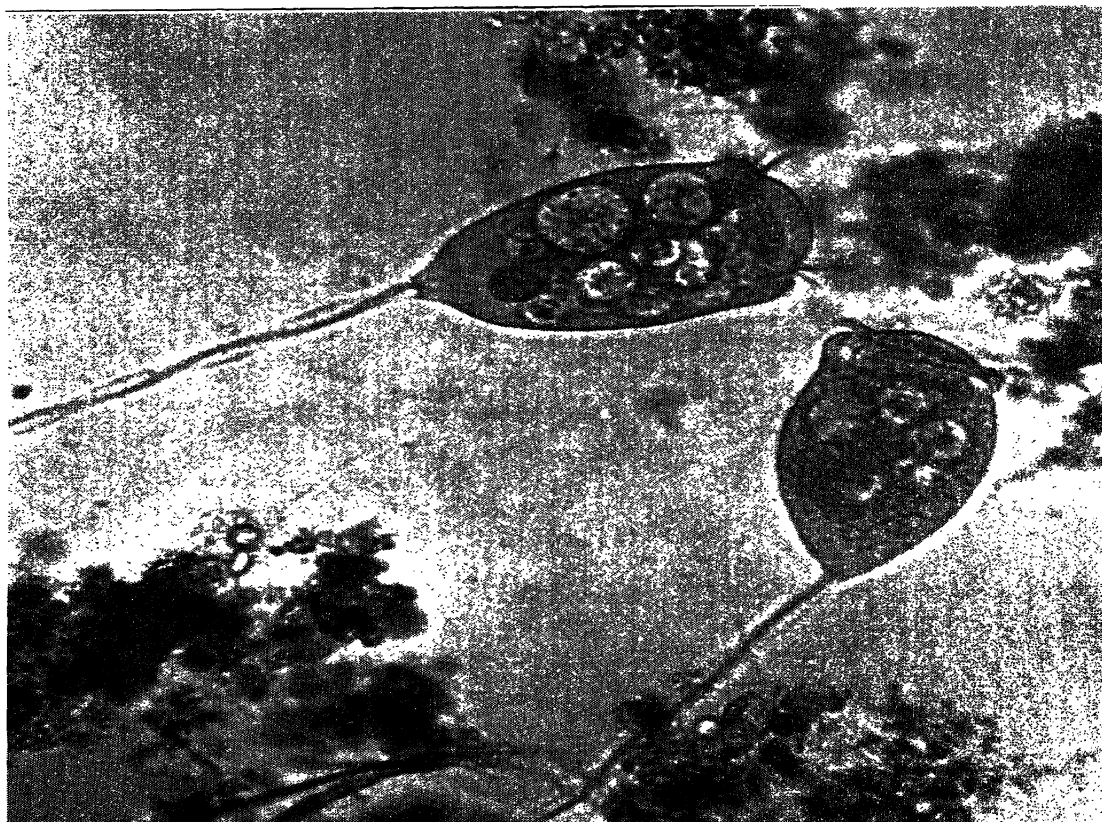
FIGURE 84.—Vorticella attached to sludge particles (400 ×); one of the protozoa in activated sludge. (Courtesy of Mr. Robert Cramer, Consulting Engineer, Milwaukee, Wis.)

sewage passes through grit chambers, then through fine screens, to reach an overflow chamber leading to the mixing channel. Here 25 per cent conditioned sludge enters and joins the raw sewage; this is now mixed sewage.

Filtered air is blown in, and the aërated mixed sewage passes to one of 12 double aëration chambers, open tanks 250 feet long by 85 feet wide. The mixed liquor is 15 feet in depth, and continues to receive air through diffuser plates located in the bottoms of the tanks. The volume of air blown in is just sufficient to produce the complete digestion. A gas con-

sisting of carbon dioxide and methane rises in sufficient volume to form a foam at the surface. Each aëration tank delivers its charge, after any one part of it has spent 6 hours in the tank, to a large sedimentation tank in which a Dorr classifier works; the clear, slightly colored effluent passes out to the lake and is called the outfall. Continuously also the classified mud is pumped in slurry form to a battery of 24 Oliver continuous filters with 14-foot drums, where it is dewatered. Automatic conveyors deliver the moist mud to rotary driers, which it leaves ready for packing. It is used as fertilizer under the name Milorganite, which analyzes 7 per cent nitrogen as NH_3, and 2 per cent available phosphoric acid.

A portion of the sludge is conditioned by additional aëration, and is used to inoculate the raw sewage.

The plant treats on the average 85 million gallons per day of a strong industrial sewage averaging close to 300 ppm. suspended solids.

A recent study [12] on the conditions necessary for the clarification of sewage as obtained in the activated sludge process indicates that there must be (1) aërobic bacterial life, (2) live protozoa, and (3) oxygen in solution. The protozoa are organisms of zoological type, and among them may be mentioned the vorticella which is attached to a sludge particle by a stem. (*See* Figure 84.)

The process of clarification from the colloid standpoint consists partly in the assimilation of matter in the colloidal state (albumen, mucin, protein, algal matter) and of dissolved organic bodies by the protozoa and bacteria, partly in their oxidation, due also to the presence and activity of the organisms. Because of the colloidally protective function of albuminous matter and of dissolved organic substances on the suspended solids, the destruction of a small amount of the protectants permits the ready settling of a relatively large amount of solids.

The sewage disposal now (1937) being installed in Buffalo, N. Y., is of still another type. The sewage is collected in large settlers located on Bird Island; the solids are settled out; the clear outfall is chlorinated and passes out to the river. The settled solids are dried and incinerated.

OTHER PATENTS

1,515,007 and 1,586,764, on the formation of zeolite mass; 1,820,978, digestion of coarse substance left on sewage screen; 1,820,977, complete sewage treatment plant with submerged aërators; 1,820,976, using activated sludge to prevent acid fermentation; 1,722,945, acceleration of sludge digestion by allowing it to settle and then raising the heavy parts and allowing it to settle a second time; 1,790,975, treatment of sewage by the activated sludge process; 1,779,810, a method and plant for the drying of sewage sludge; 1,642,206, apparatus for the treatment of sewage by the activated sludge process; 1,690,682, keeping the hard, floating sludge submerged by inserting a cover in the digestion chamber; 1,696,846, sewage treatment with a screen acting like a filter; 1,700,722, sewage treatment by activated sludge in combination with a preliminary tank treatment.

PROBLEMS

1. Filter alum, commercial aluminum sulfate, with 16 per cent Al_2O_3 content, is added to a municipal water supply at the rate of 62 pounds per million gallons.

[12] "The rôle of protozoa in activated sludge," Robert Cramer, *Ind. Eng. Chem.*, **23**, 309 (1931).

The daily volume pumped is 190 million gallons. The alkalinity is sufficient to precipitate all of the aluminum in the form of its hydrate. How much filter alum is added per day, what is the weight of the alum floc formed (on dry basis)?

2. If the alum used in Problem 1 had to be precipitated by soda ash, 98 per cent pure, how much soda ash per day would be required?

3. The chlorine is added at the rate of 2 pounds per million gallons. Over the year, with chlorine 2 cents a pound, how great is the expenditure for this item?

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Until recently, the possession of coal fields was needed to insure security and industrial prosperity to a nation; with the advances in water power and the finding of petroleum in certain coal-poor states, a partial independence of coal has resulted. And still, coal as a source of illuminating gas, dyes, and certain explosives, remained, for a while, without substitute. This is no longer so; benzene is made in huge quantities by pyrolysis followed by polymerization from petroleum gases and natural gas; dyes and explosives may rest on this source. Coal therefore seemed neatly shoved down as to its industrial irreplaceableness. Once again the wheel turns, and as a source of motor spirits by hydrogenation, coal assumes anew a front rank position, to become a comfort to the nations which possess it. Ammonia had its source in coal, forty years ago; the greatly increased amounts of ammonia now marketed and consumed are made synthetically, from atmospheric nitrogen, a store available to all. Thus does modern science offer compensations to nations not favored by a full list of natural resources.

Chapter 14
The Distillation of Coal for Gas, Coke, Tar, and Ammonia

The chief use of coal is as a fuel, as described in Chapter 12 preceding; but a higher use (economically) can be made of this material, or at least certain grades of it, by separating from it those portions which may be used in other more specific processes, and burning only that portion of the coal which cannot be so used. Also, it may be transformed into other forms of fuel, more valuable merely because of their greater convenience of application and transportation. The processes used are all destructive distillations, performed in the absence of air.

Coke which is made from the proper mixture of coals and heated long enough is a hard, strong material, the "metallurgical coke" used in blast furnaces. It is made by the distillation of coking bituminous coal, in beehive ovens, in retorts, or in the by-product coke ovens of more recent development. In 1935, 35,141,261 tons (2000 lbs.) were produced, and of this amount, 2.61 per cent were beehive oven coke. There has been a decrease from the original 100 per cent production in beehive ovens to this low figure, as gradually the by-product coke became acceptable to the metallurgical trade.

In the beehive process, coke is the sole product; a part of the volatile matter is lost outright, another part serves merely as fuel. In the by-product installations the volatile part is collected, the combustible gas is purified from ammonia, tar, vapors such as benzene, which are all recovered and utilized.

In the municipal plants, coal is distilled in retorts, primarily for its gas. Originally, the coke produced was dumped onto the grates, to fur-

nish the heat to the retorts above; but when there is a market for the coke as domestic coke, the heat is obtained by means of producer gas. In the modern plants, the retorts are vertical, and circular or rectangular in cross-section.[1] The operation of coking is continuous; coal enters at the top, by gravity; coke is withdrawn at the base, periodically, through water-sealed valve. The Woodall-Duckham vertical continuous retort
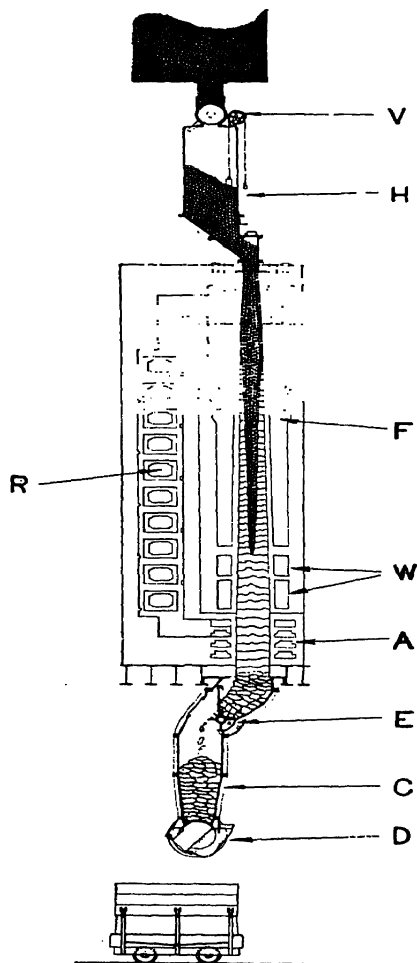
FIGURE 86.—The Woodall-Duckham vertical continuous retort (left). The gas passes out by an offtake situated just in front of the coal magazine. [Courtesy of Jerome J. Morgan, publisher, Maplewood, N. J., and The Isbell-Porter Company, Newark, N. J.]
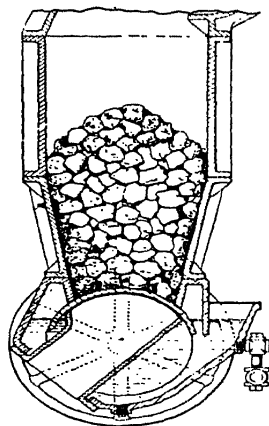
FIGURE 85. — Water-sealed gas-tight door (above). For discharging, the curved steel sheet just under the coke, is rotated to the right and down, out of the way. [Courtesy of Jerome J. Morgan, publisher, Maplewood, N. J., and The Isbell-Porter Company, Newark, N. J.]

will serve as an example. It is 25 feet high, about 4 feet by 8 inches at the top, 4 feet by 20 inches at the base, hence a narrow chamber, wider at the base, so that the coke works down of its own weight. It is built of silica bricks, and is heated by burning producer gas with preheated air in flues provided in the wall. The temperature at the wall is 2500° F. (1371°

[1] The Glover and West, and the Woodall-Duckham.

C.), while the temperature of the coke itself is 1300-1400° F. (704-706° C.). The through-put of coal is $7\frac{1}{2}$ tons per day. Steam (10 per cent by weight based on the coal) is blown into the retort at a constant rate, so that a mixture of water gas and coal gas is the product. Per ton of coal, about 12,500 cu. ft. of gas are collected. Four retorts form a bench, 5 benches on each side of an aisle form an average unit.

The coke is worked out by a slow-moving helical grate, and reaches a quenching box, from which it is discharged by a hand-operated semi-barrel valve.

The gas is purified from tar and ammonia, which are recovered, so that the plants belong to the by-product class. For small installations, they are very satisfactory; for large cities, the by-product coke ovens such as the Otto, Semet-Solvay, and Koppers are more economical, in spite of a higher first cost.

By-product Coke Ovens

For modern plants of large capacity, the oven is a narrow vertical chamber with silica-brick walls; the chamber is 28 to 39 feet long, 14 feet high, and has an average width of 14 to 18 inches. It is wider at one end (19 inches) than at the other (17 inches), in order to prevent a jamming of the coke when discharging. Heat is supplied by burning gas on the outer side of the chamber walls. A number of ovens (such as 60) form a block; the operation is intermittent per oven, but continuous for the block. The period of heating varies; an average is 17 hours.[2] The temperature in the flues, that is, at the outer side of the chamber wall, lies between 2150° and 2550° F. (1177° and 1400° C.); the temperature of the coal within the chamber is less, perhaps 1800° F. as maximum (982° C.) would be a fair average. These are the temperatures found in the general practice, which is termed high-temperature carbonization, in contrast to many proposals for working at lower temperatures, referred to as low-temperature carbonization processes; these latter are discussed briefly further on. Generally the air for combustion is preheated, the gas is not. The outgoing gases furnish heat to regenerating chambers, of which there are two per oven. The direction of the air and of the fire gases is reversed every 15 or 20 minutes; a scheme for reversing is illustrated in Chapter 11. At the end of the distillation period, the red-hot mass of coke is pushed out of the oven in a single stroke of a ram, in the short space of 3 minutes; as the ovens are elevated, the coke falls into a special car on railway tracks. The car is pulled to the quench hood, and there quenched by water. It is then dumped to a sloping platform which leads to belt conveyors; these bring the coke to screens. chutes, and railway cars for shipment. The oven charge is 11 tons of coal, or more.

In the arch forming the roof to the oven, 4 charging holes are pro-

[2] The coke oven engineers speak of "inch-hours," obtained by dividing the period of coking in hours by the width of the oven in inches; hence it is the number of hours per inch. The effort is to reduce it.

vided, with a fifth opening for the escape of the gases; this latter opening carries a cast-iron goose-neck, which reaches into a horizontal steel trough running the length of the block, the "hydraulic main." The gas from all ovens is collected in this main and conveyed by extensions to the coolers, purifiers, and meters; the liquid in the main, tar, overlaid by an impure ammoniacal water solution, serves as a seal to each retort, so that while one is being discharged, the gas does not escape, neither
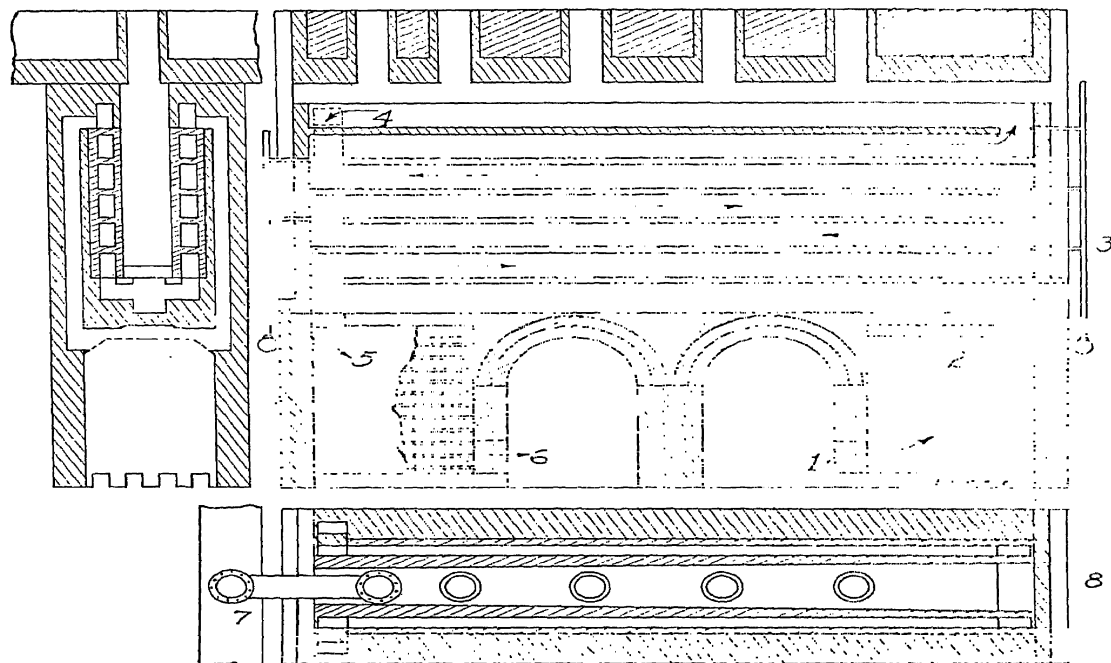
FIGURE 87.—*Upper right,* vertical cross-section, lengthwise, through the Semet-Solvey by-product coke oven, showing the heating flues. Air from tunnel 1 enters the hot checkerwork in regenerator 2, and passes along the flues and upward, burning the gas which enters through burners 3; the fire gases descend at 4 through a vertical channel to regenerator 5, and to the stack through tunnel 6. *Upper left,* vertical cross-section, crosswise, showing flues and oven proper. *Lower right,* horizontal cross-section showing width of flues and taper of oven, also the four charging holes and the hydraulic main connection at 7; the ram enters under 7, the coke drops off at 8. For dimensions, *see* text.

does air enter. The front and back of the oven are closed by cast-iron doors lined with silica bricks; when reset after discharge, they are luted with mud to make them gas-tight.

The coal is charged from a special car traveling on tracks laid on the roof of the ovens. The coal is carefully chosen, and nearly always a mixture of two kinds is used, in order to obtain a coke which will be suitable for metallurgical purposes. The mixture may be 20 per cent

of a low-volatile coal (16-18 per cent volatiles), and the rest a higher-volatile coal (30-35 per cent volatiles) with coking properties. The coal is crushed by rolls followed by a swing-hammer mill [3]; it is conveyed to a bin sufficiently elevated so that the traveling charging car may be loaded by gravity.

Dry Quenching of Coke. The heat in the coke and hot gases represents 70 per cent of the applied heat. When the hot coke is quenched with a stream of water, as is the custom, its sensible heat is wasted. Attempts have been made to substitute "dry quenching," by circulating an inert gas over the coke and under a boiler; in one trial which has been reported,[4] a recovery of 70 to 75 per cent was made.

Cooling and Purifying the Gas. Assuming that the gas is to be sold to a municipality, it must pass certain tests of purity, and on burning must furnish 537 Btu.[4a] per cubic foot. Formerly a candle-power requirement was also made, usually 18 candle power; the tendency is to abolish it because the gas flame alone is now rarely used for light. The purification leads to the collection of the by-products, tar and ammonia. The appreciable content of benzene and homologs would not need to be removed, but since the purpose of these ovens is to provide by-products, they are scrubbed out of the gas by oil. The removal of benzene lowers the candle power, but as this requirement is gradually disappearing, the gas remains salable. There is left in the gas a hydrogen sulfide impurity, which is removed by contact with wood shavings coated with lime and iron oxides, or by "liquid purification."

Coolers. The gas leaves the oven at rather moderate temperatures, for the greater part is evolved in the early stages of the coking. Some cooling takes place in the hydraulic main and its extensions leading to the cooler proper, so that it generally reaches the latter with a temperature of 170° F. (77° C.). The coolers consist of steel towers, with wooden grids; the gas comes into direct contact with the cooling liquid, a solution of ammonia, which is itself cooled in pipes sprayed with water and recirculated. A gain in liquor occurs, for the gas holds less moisture cold than hot; this excess is sent to the ammonia still. The cooled gas is drawn by centrifugal exhausters from the cooler and pressed (warmed somewhat by the compression) past the baffles of a tar extraction box into the ammonia scrubbers.

Ammonia Extraction. *a. By scrubbers.* The gas rises in a steel box filled with grids, meeting a descending stream of weak ammonia liquor; from the first box it reaches a second, and a third, fourth and fifth, losing its ammonia. The liquor from the first tower (with respect to gas travel) is the strongest solution of ammonia; the fifth tower receives water, and its liquor is fed to the fourth tower and so on. The cleaned gas passes to the benzene scrubbers. The ammonia is present in

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[3] Chapter 44.

[4] "Dry quenching of coke," D. W. Wilson, *Proc. Intern. Conf. Bituminous Coal, 2nd Conf.,* Pittsburgh, Pa., 2, 685 (1928).

[4a] New York State Public Service Commission standard.

the form of ammonium hydroxide and of ammonium salts, sulfides, carbonates, and others.

b. By direct sulfate formation. This method renders the subsequent distillation in a still unnecessary, and is therefore being adopted in all the newer installations. All the gas passes through a sulfuric acid solution, where the ammonia is retained and precipitated as ammonium sulfate. The slurry is continually pumped out (by a small steam-jet pump), the salt centrifuged, and the mother liquor returned to the absorption box with additional sulfuric acid.

Benzene Recovery. After losing its ammonia, the gas travels upward through tall steel towers with grids, meeting a stream of "straw oil" which takes up the benzene and toluene from the gas. The charged oil is distilled, the benzene collected and sold generally as motor spirits, and the free oil used over again. As a rule, two towers work in series.

Purifying Boxes. The gas next enters the base of wide, low boxes which contain the iron oxide and lime impregnated on wood shavings; hydrogen sulfide is retained, forming iron sulfide. After a period, the mass must be exposed to the air, to be revivified. A certain number of such exposures cause an accumulation of sulfur in the free state, and the mass may be used as a source of sulfur for sulfuric acid manufacture.[5]

The Thomas Meter. There remains now only the metering of the finished gas and the testing of its heat value. The device generally adopted for metering is the Thomas meter (Figure 88) in which a measured
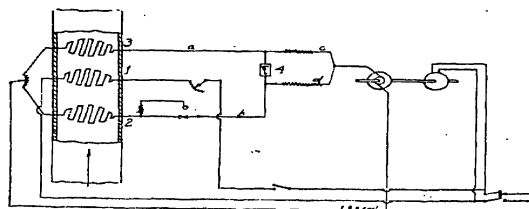
FIGURE 88.—The Thomas meter for measuring the volume of gas flow; 1, heating coil; 2, thermometer for entering gas; 3, thermometer for outgoing gas; 4, galvanometer in the Wheatstone bridge *abcd*.

quantity of electrical current, sent into a resistance-wire heating coil, is so varied that a differential of 2° F. is maintained between the temperatures of the entering gas and the gas which has passed the coil. It is the variation in this heating current which forms the basis of the measurement. The temperatures of the gas affect the resistance of two nickel wire grids which form part of a Wheatstone bridge. With the standard heating current and standard flow of gas, their resistance ratio is definite; any change in the flow disturbs the balance, and more or less current enters the heating grid by the aid of a small motor-driven regulator. The instrument is automatic and recording, and is graduated to read cubic feet directly.[6]

[5] The oxide is burned and the sulfur dioxide sent to chambers; carbon dioxide is evolved in the burning also, and tends to render the operation of the chamber very difficult.

[6] The Cutler-Hammer Manufacturing Company, Milwaukee, Wis., publication T-4. The calorimeter is reproduced in *Ind. Eng. Chem.*, 18, 1088 (1926).

The Thomas Calorimeter.   The heat content of the gas is measured continuously by the Thomas calorimeter, and the readings are recorded automatically on a chart indicating Btu. per cubic foot.[6]

Yield.   The amount of gas, coke, and other materials obtained from 1 ton of coal vary with the kind of coal used; as a guide, the following figures may be given:

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1 ton of coal produces 10,000 to 11,000 cubic feet of gas
                       1400 to 1500 pounds of coke
                       10 gallons of tar
                       18 to 30 pounds ammonium sulfate
                       2.7 gallons motor spirits.
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A large portion of the tar is obtained from the hydraulic main, the liquid contents of which are allowed to overflow to the decanter, where the tar forms a lower layer, the ammoniacal liquor an upper layer.
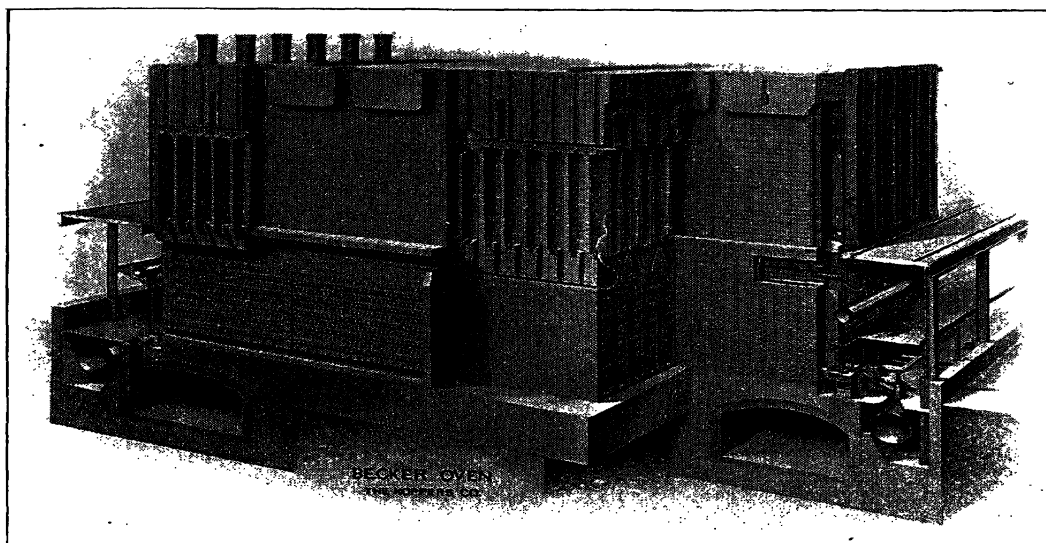
FIGURE 89.—A view of several vertical cross-sectional cuts through the Becker oven, showing: The two arched canals for air; the regenerators; the heating gas lines; the vertical flues with cross-overs; several ovens, and their charging inlets. The heating flames travel up on one side of oven, and down on the other, to enter the regenerator. As shown, the gas is not preheated in the coke oven structure. (Courtesy of the Koppers Construction Co., Pittsburgh, Pa.)

In the Koppers oven, the flues in the chamber wall are vertical, and connected by cross-over channels to the flues in the opposite wall, where the fire gases descend and pass out to a regenerator.   (*See* Fig. 89.)

Other ovens are the Otto, the Wilputte, Foundation, Piette, and Roberts.

The combination of a water-gas plant[7] and a coke-oven gas plant is not infrequent; the gases are sometimes mixed, or the water gas may be burned in the flues of the oven, thereby releasing the equivalent volume of coke-oven gas for sale.

Liquid Purification. A new method for gas purification has been installed in several plants and has proved successful. It will replace the purifying boxes filled with the lime-iron oxide shavings, or both devices may be used; in the latter case, the oxide boxes, which receive the gas already purified by the liquid process, would require refilling only at long intervals. The process is as follows:[8] The gas passes upward in a tower with wooden grids, meeting a 2 to 5 per cent sodium carbonate solution. Hydrogen sulfide, carbon dioxide and hydrogen cyanide are retained in the liquor, while the clean gas passes on. The foul liquor is pumped to the top of a second tower, while hot, and meets a blast of air which travels upward, driving out hydrogen sulfide, hydrogen cyanide, and carbon dioxide. The reactions which take place are given below; they are reversible, and run to the right while the gas passes, but to the left while the air is blown in.

$$Na_2CO_3 + H_2S \rightleftarrows NaSH + NaHCO_3; \quad Na_2CO_3 + CO_2 + H_2O \rightleftarrows 2NaHCO_3;$$
$$Na_2CO_3 + HCN \rightleftarrows NaCN + NaHCO_3.$$
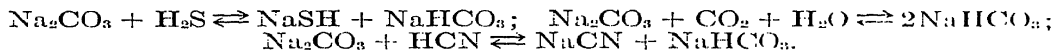
The gases passing out of the liquid purifying agent may be burnt under a small fire, to prevent a nuisance. Instead of driving out the gases, the sulfur may be recovered by the Thylox process,[8a] in which hydrogen sulfide from the gas is retained and, in a subsequent step, transformed into elemental sulfur. A solution of sodium thioarsenate

$$Na_4As_2S_5O_2 + H_2S \rightarrow Na_4As_2S_6O + H_2O$$
absorbing reaction
$$Na_4As_2S_6O + O \rightarrow Na_4As_2S_5O_2 + S$$
revivifying reaction
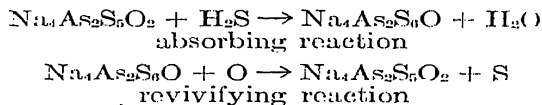
accepts the hydrogen sulfide; on blowing with air, part of the sulfur in the latter compound is liberated, and comes to the top of the solution; it is skimmed off and filter pressed. In this change due to air, the first compound is reformed, and is ready for new absorption. Sulfur in this extremely finely divided form has proved to be a valuable fungicide.[9]

Triethanolamine (Chapter 25) instead of soda ash has been used in the liquid purification method for coke oven gas; after the absorbing liquid has taken up all the impurities it can hold, it is treated with steam which revivifies it, restoring it to its original state.[10] Triethanol-

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[7] Chapter 15.

[8] U. S. Patents 1,389,980 and 1,390,037. *See also* the Petit process, in which a solution of potassium carbonate is recommended, and essentially the same reactions take place; described on p. 537, "Modern Gashouse Practice," Alwynne Meade, London, Ernest Benn, Ltd., 1921.

[8a] "Chemistry of the Thylox purification process," H. A. Gollmar, *Ind. Eng. Chem.*, **26**, 130 (1934).

[9] *Ind. Eng. Chem.*, **25**, 364 (1933).

[10] "Organic bases for gas purification," R. R. Bottoms, *Ind. Eng. Chem.*, **23**, 501 (1931).

amine is a high boiling liquid, strongly alkaline; it is used over and over again. Figure 90 shows the apparatus employed.

Sodium Phenolate Gas Purification. Still another gas purification by means of liquids must now be added to the list. It is the phenolate process, designed for the specific purpose of ridding refinery gas or natural gas of any hydrogen sulfide it may contain, an admixture which is frequently high. The absorbed hydrogen sulfide is liberated in the actifier, in concentrated form, and becomes the source of sulfur for the manufacture of sulfuric acid, displacing a corresponding tonnage of brimstone which otherwise would have to be bought. The phenolate process is

FIGURE 90.—Liquid purification of illuminating gas, using triethanolamine, with revivification of the absorbent by heat. (Courtesy of Mr. R. R. Bottoms, the Girdler Corporation, Louisville, Ky.)
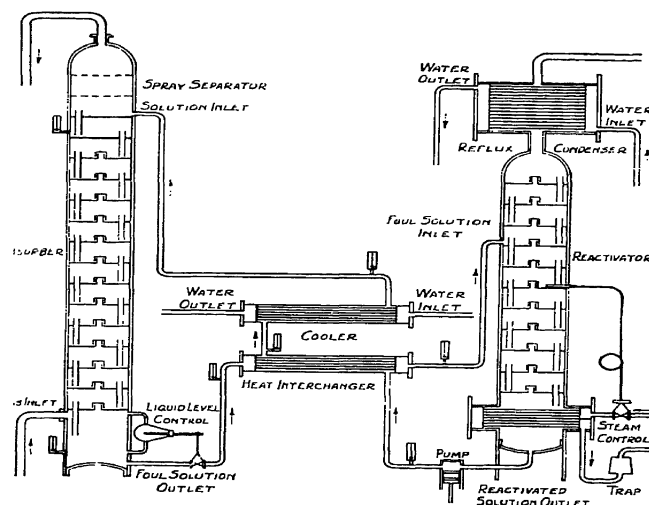
timely, for by its means refinery and natural gas may be placed in the state of purity required for the pyrolysis and polymerisation into synthetic gasoline.

In the Koppers phenolate process [10a] the refinery gas or natural gas rises in the plate column absorber, meeting a descending cold liquid, a solution of phenol in caustic. Essentially all the hydrogen sulfide present in the gas is absorbed (96 to 99.8 per cent). The charged solution passes through a heat exchanger, taking heat from the hot liquor leaving the actifier, and enters at the top of the latter, also a plate or bubble-cap tower, only somewhat larger than the absorber. As the charged solution descends, it meets steam rising from the lowest portion of the solution which lies in contact with a steam chest. The hydrogen sulfide with steam leaves the actifier overhead, passes two dephlegmators, and thence to a burner for the production of sulfur dioxide. The liquor leaves the actifier

[10a] "Koppers phenolate gas purification process for recovery of sulfur from natural and refinery still gases," the Koppers Construction Company, Pittsburgh, Pa.; also U. S. Patents 1,971,798, 2,002,357, 2,028,124, 2,028,125.

hot, and free from hydrogen sulfide; it passes an exchanger and a cooler, and then enters the absorber, at the fourth plate from the top (12 plates in all). Fresh water is added continuously to the top tray of the absorber; the three top trays become, in effect, a water scrubber to retain entrained chemicals. At stated intervals (one week) chemicals lost to the system are replenished.

The high carrying capacity of this solution makes it possible to pump only 5 to 10 gallons of solution per 1,000 cubic feet of sour gas; this is a low ratio, which means economy of installation and operation.

MODERN PRACTICE IN COAL-TAR DISTILLATION

In recent years, the distillation of coal tar has received much study and attention, and a number of improvements have been made.

The aim of the tar-distiller is to produce as much oil as possible (from which, then, more of the valuable constituents may be isolated), with a pitch having a high melting point, and at the same time to keep
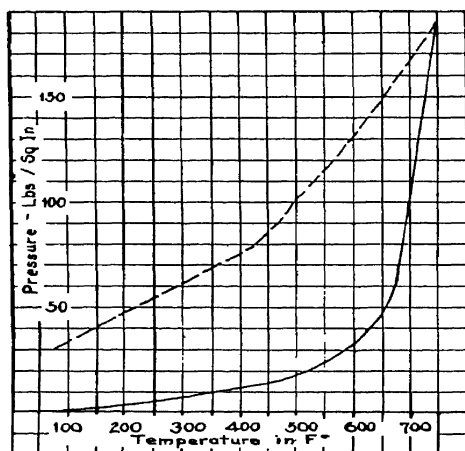
FIGURE 91.—The effect of heat on tar. Full curve, heating tar in autoclave; dotted curve, cooling same autoclave; the higher pressures are due to evolved

down the formation of free carbon. The higher the temperature, and the longer the tar is subjected to it, the more gas forms, and the less oil. The aims have been therefore to reduce the time of heating, to agitate the tar layers in contact with the heating walls, or to operate in novel ways, avoiding all the old defects. A batch still is a steel vessel heated by an open fire; instead of heating only the lower half, all of it may be heated, reducing the recondensation on the cooler upper walls. The improvements include: modified batch stills, such as vacuum stills, stills with steam agitation, inert gas recirculation, and coke stills, in which the residual pitch is heated until only coke remains [11]; pipe or tube stills, consisting of a coil of pipe set in a furnace, and through which the tar

[11] U. S. Patent 1,230,782.

passes continuously; the coke-oven tar still, which is built on top of the coke-ovens, and employs lean coke-oven gas as source of heat.

As the heating of tar progresses, permanent gases are evolved, the free carbon content rises, and the melting point of the resulting pitch increases. The evolution of gases as measured by pressure is shown in Figure 91 [12]; it will be observed that changes are slow below 600° F. (315° C.), and rapid above 700° F. (371° C.). The increase of cracking as the temperature is increased is evident. The free carbon increase is 15 per cent.

The improved recovery of oil in vacuum stills is shown in Table 25.[12]

TABLE 25.—*Vacuum Stills vs. Atmospheric Stills.*

Stills	Temperature °C.	°F.	Oil	Pitch	Free Carbon
			Per cent		
Vacuum	330	626	56.6	42.5	28.8
Atmospheric	413	775	40.1	57.8	40.7

In the pitch from the atmospheric distillation the free carbon is 2.8 times that to be expected by the simple concentration of the free carbon present in the original tar; while in the vacuum still the increase is 1.4 times. In the stills with steam agitation, the improvement is similar.

The inert gas circulation system [13] (*see* Fig. 92) has the great advan-
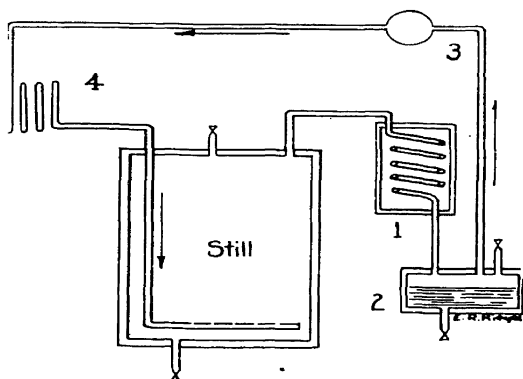
FIGURE 92.—Diagrammatic scheme for the inert gas recirculation process for distilling coal tar. 1, condenser; 2, receiver and separator, the gas passing out to pump 3; 4, heater.
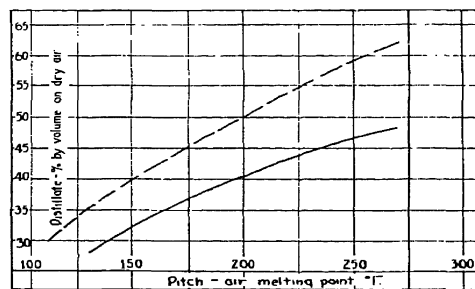
FIGURE 93.—Percentage distillate and corresponding pitch melting point from a tar still with inert gas circulation.

tage of being adaptable to any batch still; the improvement in amount of distillate and, at the same time, higher melting point of resulting pitch is well shown in Figure 3. At first, nitrogen or carbon dioxide was used,

[12] "The distillation of coal tar," by John M. Weiss, *J. Soc. Chem. Ind.*, **51**, 219 (1932).
[13] U. S. Patent 1,418,893; related schemes in U. S. Patent 1,800,224.

and the rate was 0.33 cu. ft. of gas per gallon of tar per minute for carbon dioxide, and 0.40 cu. ft. per gallon per minute for nitrogen. A sample of the results [12] is shown in Table 26.

TABLE 26.—*Inert Gas Circulation System vs. Atmospheric Distillation.*

System	Temperature		Pitch		Oil	Free carbon
	° C.	° F.	Per cent	M. pt.	Per cent	Per cent
Atmospheric still	413	775	57.8	280° F. (138° C.)	40.1	40.7
Recirculated CO_2	358	677	46.9	277° F. (136° C.)	52.6	29.0
Recirculated N_2	331	628	46.4		52.0	27.2

It was found that if air is recirculated, its oxygen is soon consumed, and the residual gas is in effect inert. The method has been adapted to stills of capacities varying up to 10,000 gallons.

A very recent improvement has been the placing of the distilling vessels on top of the coke-ovens,[14] and utilizing the lean coke-oven gas as a source of heat. Only the sensible heat in such gas is used, and after contact with the tar, it rejoins the main flow of gas and yields its combustion heat elsewhere. The cost for fuel is thus nil. Another advantage is that the crude tar need not be transported; any fractions which must be burned are so used on the premises; only the parts for which there are orders are made to bear a shipping charge.
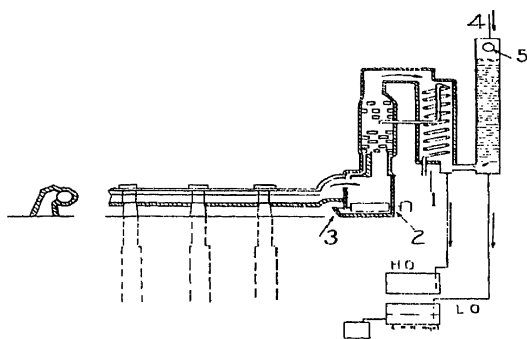
FIGURE 94.—Tar still using the sensible heat of lean coke-oven gas. 1, entry for tar; 2, rotor roll to splash pitch; 3, draw-off for pitch; 4, entry for weak ammonia liquid; 5, outlet for cold gas.

The procedure is indicated in Figure 94. The tar is preheated in the coil marked 1, and is delivered in spray form into the distilling tower, passing downward. The hot coke-oven gas passes upward, volatilizing the oils, but allowing the pitch to pass down to the distilling main; in the latter a rotor roll works and splashes the pitch into the incoming gas. Periodically, pitch is withdrawn at 3. The gas leaves the tower laden with oil vapors; it deposits the heavy oils while in contact with the coil bringing the new tar. The light oils are recovered in the final tower, packed with rings, down which a cold ammoniacal water solution flows. The condensed

[14] Can. Patent 304,941 (1930); *see also* 304,940 to 304,946.

light oil and water pass down to a separator, while the cleaned cool coke-oven gas leaves at 5 to join the main flow of gas.

This almost ideal scheme has been quite successful, except that the close control over the quality of pitch which the inert gas recirculation procedure allows is not equaled.

The oil fraction is next divided into four fractions, which contain: (1) the light oil, benzene, toluene, xylene, some pyridine and naphthalene; it forms 25 per cent of the total, and boils up to 170° C. (338° F.); (2) the carbolic oil, phenol, naphthalene, and pyridine bases; it forms 10 per cent of the total, and boils up to 225° C. (437° F.); (3) the creosote oil, cresols mainly; it forms 10 per cent of the total, and boils up to 270° C. (518° F.); (4) the heavy oil, anthracene, phenanthrene, carbazol, forming 40 per cent of the total, and boiling up to 320° C. (608° F.). The boiling points given are those observed at atmospheric pressure; at reduced pressure, or with inert gas circulation, they are correspondingly reduced.

The refining of these fractions constitutes an important industry, partly because it furnishes the raw materials for the dye manufacture, partly because its products are the basis for some of the military explosives which must be obtainable within the borders of the country for the emergency of national defense. The purification is mainly by distillation, caustic treatment, and sulfuric acid washing.

The processes are as follows [15]:

(1) The light oil is distilled in fire-heated fractionating stills under reduced pressure; the shelves of the fractionating column have small cones and bells so that the rising vapors must bubble through the liquid. The products are crude benzene, crude toluene, crude solvent naphtha, and a residue of tarry nature which serves as fuel.

The various crude products are washed with sulfuric acid, then with caustic solution, and again distilled by themselves in steam-heated stills with columns, at atmospheric pressure. Pure benzene, toluene, and xylene are obtained; per ton of coal, the yield is 0.4 gallon toluene, 2 gallons benzene, and 0.2 gallon xylene.

(2) The carbolic oil is cooled in large shallow pans, where the naphthalene separates in the solid state; it is centrifuged to form crude naphthalene. The oil which remains is washed with caustic, removing the phenol; then with dilute sulfuric acid, in order to dissolve the pyridine bases; the residue is distilled and gives essentially two parts, solvent naphtha, the distillate, and a resin (cumar) which is left in the still. The caustic solution is acidified to free the phenol, and the latter is distilled in fire-heated stills at reduced pressure; the product is a crude phenol, which must be redistilled in steam-heated stills. This distilled product is refined still further by mixing it with a little water, cooling it to a cake, crushing this, and centrifuging the mass; there is finally obtained the crystallized phenol of commerce.

[15] *Chem. Met. Eng.,* **23,** 321 (1920).

The pyridine bases are recovered from their acid solution by adding caustic, and then distilled.

The crude naphthalene obtained in the first step is purified by melting, cooling again, and centrifuging the semi-solid mass which results. The cleaned solid in the basket is melted again, distilled in fire-heated stills, and the distillate agitated while melted with sulfuric acid first, then with caustic, and the residue again distilled; the distilled material on cooling solidifies and is the naphthalene of commerce.

Fraction (3) may be used as such.

(4) The heavy oil solidifies on cooling; it is washed with solvent naphtha and filtered; the naphtha contains the phenanthrene. The filter cake is next washed with pyridine, to remove carbazol. The remaining solid is sublimed and condensed in large chambers, as a white solid; it contains 80 to 85 per cent anthracene.

The pyridine solution is distilled, yielding in the distillate first pyridine, then carbazol, a solid; the latter is washed with solvent naphtha and sublimed; the product is 85 to 90 per cent carbazol.[16]

TABLE 27.—*United States Production of Certain Coal Tar Crudes 1935 (U. S. Tariff Commission).*

Tar	450,307,827 gallons	4.1 cents/gallon
Crude light oil	134,070,840 gallons	8.5 cents/gallon
Benzol	24,106,006 gallons	12.9 cents/gallon
Motor benzol	38,379,910 gallons	8.9 cents/gallon
Toluol	17,776,551 gallons	27.9 cents/gallon
Solvent naphtha	4,970,842 gallons	20.8 cents/gallon
Xylol	3,695,656 gallons	23 cents/gallon
Naphthalene	47,653,372 pounds	1.7 cents/pound
Anthracene, cumene, cresylic acid	$256,405 in value	
Creosote oil	92,869,152 gallons	10.2 cents/gallon
Crude tar acids	279,129 gallons	
Road tars	112,038,763 gallons	8.4 cents/gallon
Pitch of tar	436,570 tons	12.37 dollars/ton

Low-Temperature Carbonization. By carbonizing at a lower temperature than customary a higher yield of liquid products, resembling oil rather than tar, may be obtained. The oven wall temperature in usual practice is 2350° F. (1288° C.); in the low-temperature processes, it would be 1300° F. (704° C.) and less. The difficulty is to perform the carbonization in reasonable time; the temperature is so low that the rate of its penetration is also low. Very thin layers of coal have been tried; also carbonization by passing in hot producer gas. For the present, the low-temperature processes are not of industrial importance in the United States.[17]

Ammonia Distillation. The ammonia still shown in Figures 95 and 96 liberates ammonia gas in two distinct steps. The upper part of the tall vessel, to the right, is a six-plate tower, each plate with caps and run-down pipes. The liquor to be distilled is fed in at the top plate; the

[16] The formulas of many of these compounds will be found in Chapters 27 and 28.

[17] "Lessons from low temperature carbonization," R. P. Soule, *Proc. Intern. Conf. Bituminous Coal, 3rd Conf.*, Pittsburgh, Pa., **1**, 272-298 (1931).

free ammonia is driven out by heat alone. By free ammonia is meant ammonium hydroxide, sulfide and carbonate. At the last plate, a liquor collects which has no free ammonia, but still contains fixed ammonia, that is, sulfate or chloride, which must be treated with lime in order to liberate the ammonia gas. This liquor runs through by-pass 2 (*see* Fig. 96) to the lower part of the taller vessel, where milk of lime is sent in. Liquor and lime mix thoroughly by the time they reach the overflow to the fixed leg, where they travel downward over plates with

FIGURE 95.—Ammonia still with continuous operation. At the right, the lime leg surmounted by column for free ammonia distillation; at left, the fixed leg. *See* diagram in Figure 80. (Courtesy of the Koppers Construction Co., Pittsburgh, Pa.)
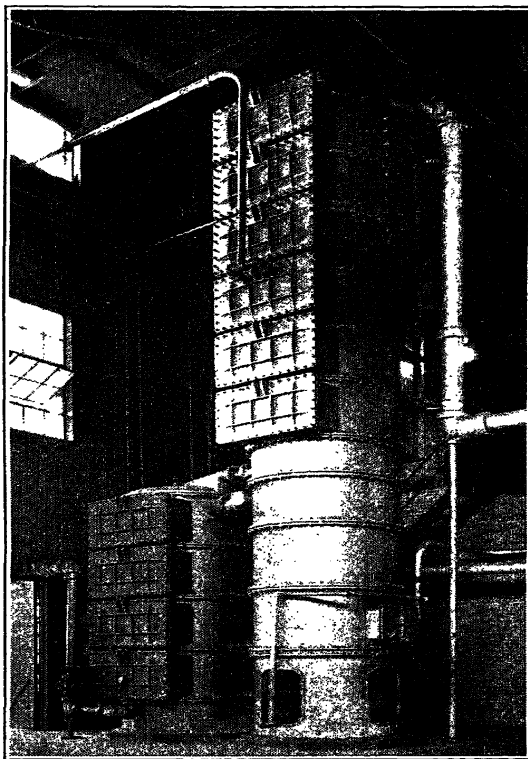
caps and through the run-down pipes to the waste pipe 7. A strong flow of steam enters near the base of the fixed leg, driving out the ammonia completely; this latter passes upward into the free still and with the ammonia from that still passes through a dephlegmator to the saturators, where ammonium sulfate is produced.

The same still may be used to produce ammonia aqua. For this purpose it is necessary to retain hydrogen sulfide and carbon dioxide; this is done by an additional caustic soda wash, in a short column with plates and bubble caps. The purified ammonia gas is absorbed in lead bottles. (*See* Fig. 97.)

In regular coke-oven practice, the ammonia still receives only a small part of the total ammonia in any form; the bulk of the ammonia in the coal passes directly to the saturators while still in the coke-oven gas, as stated under Ammonia Extraction. It is the increment in the ammonia liquor used as cooling spray which is sent to the still, together with the water layer from the condensate in secondary coolers.

Figure 96.—Operation of ammonia still with continuous operation; Koppers system. 1, liquor inlet into the free still; 2, by-pass to the lime leg or mixing vessel, receiving lime at 3 and steam at 4; the milky suspension overflows to the fixed leg, receiving steam at 5; 6, ammonia vapors outlet; 7, waste pipe to sewer.

Figure 97.— Absorption of ammonia in water, using lead absorption bottles; the rich gas enters through trap 1, bubbles through 2, then 3, finally 4, and passes out, free from ammonia, at 5; the amount passing out is very small. The water from 4 is run into 3, and this into 2, where it is brought up to strength. Each bottle has a lead cooling coil, not shown.

A certain amount of gas liquor will always have to be distilled because small gas plants scrub their gas free from ammonia by water. The resulting liquor is usually concentrated by a preliminary distillation, and sold to a chemical firm, where it is made into aqua or ammonium sulfate. In order to make sulfate, the still just described would be employed to furnish the ammonia gas, impure with hydrogen sulfide and carbonate, and this gas would be passed through a lead distributing pipe into a sulfuric acid solution partly saturated with ammonia. The salt formed may be shoveled out by hand or may be removed by a steam ejector. The unabsorbed gases are piped under a fireplace, so that only sulfur dioxide and carbon dioxide need be discharged into the atmosphere.

The reactions with lime are: $2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$; and $(NH_4)_2SO_4 + Ca(OH)_2 = 2NH_3 + CaSO_4 + 2H_2O$. In the free still, they are: $(NH_4)_2S = 2NH_3 + H_2S$; $(NH_4)_2CO_3 = 2NH_3 + CO_2 + H_2O$, and several others in small proportion.

De-phenolizing Ammonia Waste. The chlorination of city water has led at times to a bad taste, traced to a phenol content in the water, originating in the waste from the by-product ammonia still in a city gas

FIGURE 98.—Apparatus for dephenolizing ammonia liquors in coal distillation plants, by inert gas circulation (Koppers system). 1, phenol bearing liquor; 2, phenol-free liquor; 3, fresh caustic solution; 4, circulated No. 2 caustic solution; 5, circulated No. 3 caustic solution; 6, inert gas laden with phenol vapors; 7, sodium phenolate solution outlet.

E. R. Riegel
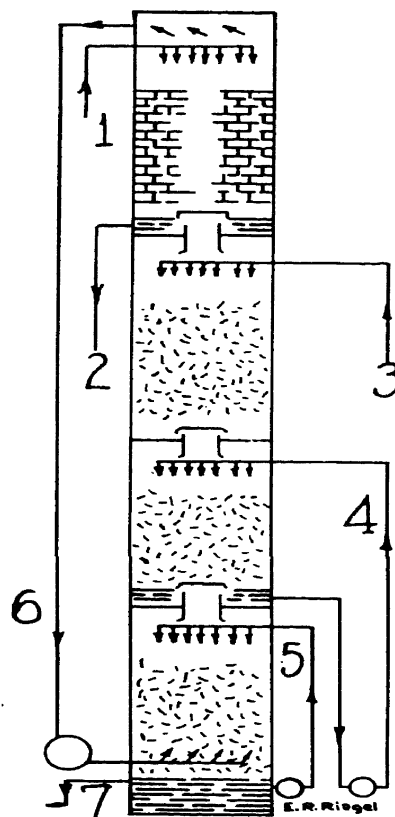
plant or in any coke plant. The phenol is removed by taking the ammonia liquor at outlet 10 in the working sketch of the Koppers still (Figure 96), and sending it through a de-phenolizing system such as shown in Figure 98, wherein the phenol is removed in vapor form by an inert gas, which then is scrubbed by caustic. There is formed sodium phenolate, which is collected and removed to a storage tank; later the phenol is regenerated by treating with an acid. The phenol-free liquor returns by inlet 11 to the ammonia still, to receive the lime treatment.

Towers in which finely divided liquid benzene rises through the ammonia water, dissolving any contained phenol, are also in use; four

unpacked towers are used, and the benzene travels counter-current to the ammonia liquor.

OTHER PATENTS

U. S. Patent 1,888,465, operation of by-product coke oven plant; 1,891,129, coke extractor for vertical (West) carbonization retorts; 1,841,036, enriched water gas and high-grade coke from caking bituminous coal; 1,838,294, coke oven battery (Becker); 1,805,922, horizontal coke oven (Otto); 1,829,608 and 1,787,490, vertical chamber coke oven; 1,787,963, coking retort oven; 1,832,181 and -2, coking retort oven; 1,832,612 and -3, coke oven (Becker); 1,893,145, on distilling tar residue by direct contact with hot gases at high temperature; 1,888,235-6, passing hot cove-oven gas through successive sprays of coal tar immediately after gas leaves the oven; 1,844,892, 1,862,494, 1,868,394-5, 1,871,550, on using by-product recovery system of coke-ovens to recover clean tar oils; 1,871,596, continuous distillation by bringing tar into indirect counter-current heat exchange relation with hot coke-oven gases.

PROBLEMS

1. A by-product coke plant disposes of 3200 gallons of motor spirits per day, which is also the daily production. Using the yield figures in the text, how much coal was distilled?

2. For the production of 315 tons of ammonium sulfate, how many tons of coal are coked, if the yield figures in the text apply?

3. In a Woodall-Duckham vertical retort, a coal is gasified which contains on analysis 19 per cent of combustible volatiles. Each ton of coal furnishes 13,350 cu. ft. of clean gas, ready for the holder. How much gas is due to the steam-on-coke reaction? (For water gas relations, *see* next chapter.) The gas from the coal proper occupies 20 cu. ft. per pound of weight.

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"The recovery of benzole by active carbon," H. Hollings and S. Hay, *J. Soc. Chem. Ind.,* **53,** 143 (1934).

Fuel in the form of gas under slight pressure offers many advantages; its distribution costs little, once the pipes are laid; it is ashless, smokeless, and its application requires very simple devices. The use of combustible gas in municipalities is increasing, in spite of the newer electrical heating devices. In the industries, gas is largely employed as a fuel.

Chapter 15

Combustible and Illuminating Gas, Water Gas, Producer Gas and Natural Gas

The typical combustible gases which are manufactured are coal gas, coke-oven gas, water gas, producer gas, and oil gas; natural gas is obtained from the earth.

Coal gas and coke-oven gas are very similar; both are made by the distillation of bituminous coal. By coal gas is meant the gas made in the smaller retorts, either horizontal or vertical, in which coal is distilled primarily for the gas it yields; coke-oven gas is made in coke ovens, with coke and gas both primary products. Coal gas is high in illuminants (benzene, ethylene); in former years, it was still higher, for the original horizontal retorts had a vapor space over the coal which was exposed to the same high heat as the coal itself, and in this space nearly all the tar and oil was "cracked," producing mainly illuminants. Since the introduction of the vertical retorts, filled over the whole cross-section with coal, less cracking takes place, and coal gas resembles more closely the gas from coke ovens, in which such cracking is also restricted.

Water gas is an entirely different product; it is made by passing steam through a bed of incandescent coke or other fuel; except for unimportant impurities it consists of hydrogen and carbon monoxide.

The manufacture of producer gas on the other hand is a continuous process; it is made by passing a mixture of steam and air into a bed of burning coke, anthracite, non-coking low-volatile coal, lignite, or peat. The resulting gas contains hydrogen and carbon monoxide as valuable constituents; nearly half of it is nitrogen, so that its heating value is low. Producer gas is used, after careful cleaning, in gas engines (internal combustion). Mond gas is producer gas made at low temperature so that the ammonia in the coal may be conserved and later recovered. Blast-furnace gas [1] is also a form of producer gas.

Oil gas is made by "cracking" [2] suitable fractions of petroleum, in districts poor in coal and lignite, but rich in oil; it is rich in illuminants and has a high heating value.

Natural gas is obtained from the soil, chiefly by means of deep wells; the gas may issue from the well under pressure, or pumping may be required. It varies in composition, frequently containing a high percent-

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[1] Chapter 47.
[2] *Compare* the cracking of oil for gasoline, Chapter 24.

age of methane, and just as frequently, non-combustible impurities; in general, its heating value is very high.

There are many combinations of two or more of these typical combustible gases; the most frequent probably is that of oil gas and water gas, produced by enriching straight water gas by carburetted oil. In Buffalo at the present time the city gas consists of a mixture of coke-retort gas, coke-oven gas, water gas enriched by oil (hence containing oil gas) and natural gas.

The composition of several typical combustible gases is exhibited in Table 28; the constituents are listed in the order in which they are determined in the analysis; the figures are percentages by volume.

TABLE 28.—*Composition of Typical Combustible Gases.*

	Straight coke-oven gas	Straight water gas	Water gas enriched by oil*	Producer gas	Natural[2a] gas
			Per cent		
Carbon dioxide CO_2	1.8	3.7	4.25	5.2	...
Benzene C_6H_6	.9	...		...	...
Ethylene C_2H_4	2.3	...		1.0	...
or other illuminants			10.33		
Oxygen O_2	.8	.5	.71	.2	...
Carbon monoxide CO	5.5	42.3	31.60	26.3	...
Hydrogen H_2	49.2	47.9	35.38	14.4	...
Methane CH_4	30.3	.6	12.40	1.8	90.0
Ethane C_2H_6	...	...	....	...	8.8
Nitrogen N_2	9.2	3.4	5.33	51.1	1.2
Total combustibles	88.2	90.8	89.71	43.5	98.8
Btu. per cu. foot	555	299	574	155.6	1110

* 3.10 gallons of fuel oil per 1000 cubic feet of gas for enrichment.

[2a] As to natural gas, other analyses will be found elsewhere in the book; it should be remembered that some natural gases contain sulfur, some contain nitrogen in sizable amounts, others helium, still others contain unsaturated hydrocarbons. For the analysis of a wood gas, *see* chapter 16.

An inspection of this table will show that the heat values of coke-oven gas and straight water gas differ markedly, yet their percentage of combustibles is about the same. The reason is that the component compounds have different heats of combustion; hydrogen evolves 329 Btu. per cubic foot, measured at 62° F. and 1 atmosphere; carbon monoxide 322, methane 1003, ethane 1755. It is possible to compute the heat value of a mixed gas from the known values of the heats of combustion of the component gases; thus for the coke-oven gas listed in the table, the calculated heat value is 556 Btu.,[3] while the observed value was 555. It may be noted also the producer gas has the lowest heat value; the same high temperatures which other gases furnish are nevertheless obtained with producer gas by preheating it in regenerators; the need of heating a vast volume of inert gases by the combustion itself is thus largely avoided.

[3] A part of this gas is distributed to townships near Buffalo, for direct consumption; it is therefore made slightly better than the New York State standard, 537 Btu.; there is no candle power standard in New York State. Another part of this gas is mixed with natural gas and water gas, for distribution in the city of Buffalo; for this purpose it could be lower, since natural gas raises its heat value.

The manufacture of coal gas and of coke-oven gas has been described in the preceding chapter.

WATER GAS [4]

Water gas is made by passing steam into a bed of incandescent coke; the temperature of such a fire is 1400° C. (2552° F.). Between the temperatures of 1400° and 1000° C. (1832° F.), the reaction $H_2O + C = CO + H_2$ takes place. As it proceeds, there is a fall in the temperature of the fire; the incoming steam must be heated. The reaction itself is endothermic, and heat is lost by radiation. With coke at a temperature below 1000° C., the steam reacts to form carbon dioxide, which is not desired, for carbon dioxide has no calorific value.

$$2H_2O + C = CO_2 + 2H_2.$$
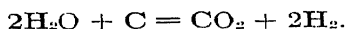
Hence the steam is stopped before the low temperature is reached, and the fire is brought back to its normal high temperature, 1400° C., by an air blast. Coke is consumed during the blast period, so that it could not be expected that all of it would be represented by carbon monoxide. Usually, between 50 and 60 per cent is transformed into the lower oxide; the rest burns to carbon dioxide which escapes through a stack. There always are a few colder spots present, so that the second reaction takes place to some extent.

For many purposes, water gas is used as such; for sale in municipalities, it is usually enriched with oil gas, produced in a separate vessel forming part of the system. The gas-making period lasts 4 minutes; the air-blast or revivifying period, 2 minutes; the complete cycle is therefore 6 minutes. In order to fully use the hottest coke, the steam period is divided in two, and the steam sent in from below for one half, from above during the other half. Simultaneously with the change of direction of the steam, one of two gas valves open, so that the gas formed is led off in either case through a wide flue to the oil-gas vessel. After the steam has been on 3 minutes, the apparatus is purged for 1 minute, and then only is the air blast turned on. The operations and their duration are then: 1½ minutes for "up-steam," 1½ minutes for "down-steam", 1 minute for purge, and 2 minutes for air blast.

The complete generating apparatus consists of 3 vessels; the generator, the carburator, and the superheater. All are steel vessels, cylindrical, of somewhat differing heights and diameters, as indicated in the accompanying figure (Fig. 99); the generator is 10 feet in diameter and 15 feet high. The coke fire is in the generator; the coke charge is shoveled in through an opening in its top, level with the working floor. The steam for the up-blow enters below the fire through a perforated circular distributor; the gas made passes out through the upper valve in the 42-inch flue to the carburator. For the down-blow, the steam enters above, and the gas passes out through the lower valve which lies in the

[4] Also called blue gas, because it burns with a blue flame.

same vertical plane as the upper; a flue leads the gas to the upper horizontal flue, so that this gas enters the carburator in the same place as the up-blow gas. The valves are slot valves, and being exactly in one plane, are operated by one rod; the three-way steam cock is connected with levers to this rod, so that a single motion (small compressed air cylinder) makes all the changes simultaneously. The generator and flues are brick-lined.

The carburator is filled with a checkerwork of bricks; during the air blast, the products of combustion stream through and raise its heat. During the steam period, the made gas. at high heat itself, enters near
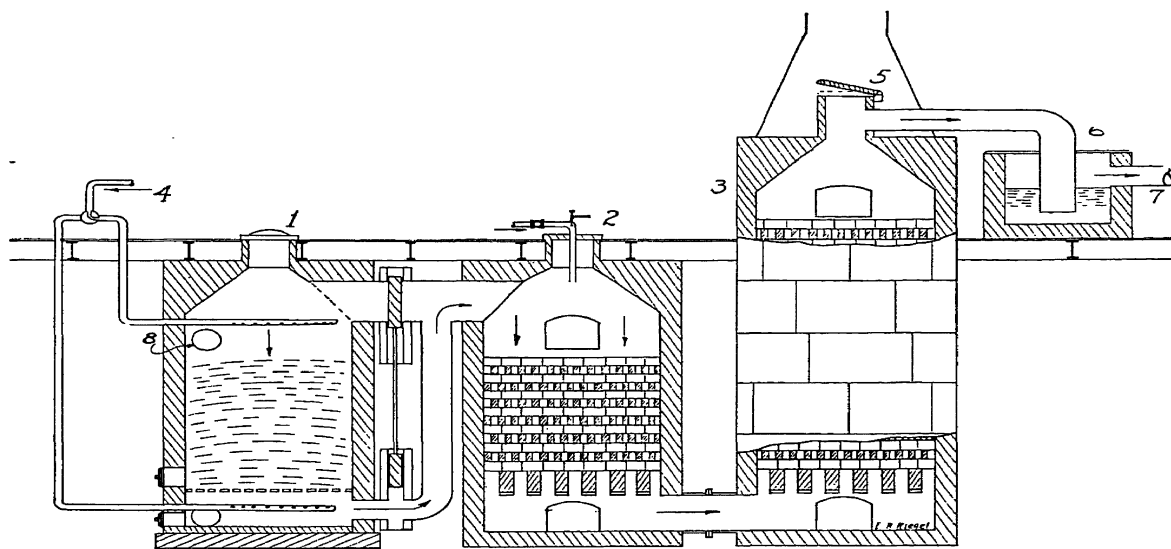
FIGURE 99.—Cross-section through a water-gas plant. 1, generator; 2, carburator; 3, superheater; 4, steam inlet set for down-blow; the path of the gases is shown by arrows; valve 5 being closed, they pass through water box 6 to conduit 7 which leads to the purifying apparatus. 8 is the inlet for the blast during the revivifying period.

the top and passes downward, while an atomizer delivers oil at the top of the carburator. The current of gas carries the mist of oil against the hot checkerwork; the greater part is reduced to molecular fragments which at normal temperature form gases; at the same time, a certain amount of tar is produced. From the base of the carburator the gases pass to the superheater, in which they stream upward, to be delivered to the flue leading to the purifying apparatus. The superheater is also filled with bricks, and provides space and heat to carry the oil-cracking and the thorough mixing of the gases as far as possible. The path of the gases is indicated in the general illustration.

The three minutes of steam blow are followed by one minute of purge, during which steam enters at the top of the carburator and sweeps

out the good gas which remains in the carburator and in the superheater. At the end of four minutes, the blast is turned on, to bring the fire back to incandescence; the products of combustion, after passing through generator and superheater, escape through a stack just above the latter, through a valve in the flue leading to the purifying apparatus. Each time the valve opens, the waste gas catches fire with an explosion-like noise. Safety of operation is insured by interlocking devices, which permit the opening and closing of the several valves only in the proper order.

For the generator of the dimensions given, coke of the egg size is introduced in 820-pound lots; the production is about at the rate of 1000 cubic feet of straight water gas to each 40 pounds of coke consumed (total). To enrich this gas, varying amounts of fuel oil or special gas-oil fraction are used, for instance $3\frac{1}{2}$ gallons per 1000 cubic feet of water gas; in the set described, this would require 20 gallons per cycle. The temperature in the carburator lies between 1200 and 1300° F. (650° and 704° C.), and is measured by means of pyrometers.[5]

In an oil-gas plant, a generator and superheater are used, and the heat is furnished by an oil burner; otherwise the operation is similar to the one just described.

The Purification of Carburetted Water Gas. The flue leading away from the superheater dips in the water of the wash-box, where the small amount of tar is deposited; the gas then passes to the cooler, a nest of pipes laid in running water. From here it is pulled by exhausters and pushed into the purifying boxes containing the same lime-iron oxide coated shavings which are used for coke-oven gas.[6] From the purifying boxes, the gas passes to the holders, ready for delivery. Metering and testing are performed by the continuous, recording Thomas meter and Thomas calorimeter already described (Chapter 14).

A water-gas plant is compact; it may be started at short notice, and when shut down for a given period is readily maintained in good condition. When part of a system supplying municipalities, it is usually shut down in the summer months, when the demand is light enough to be supplied by coke-oven gas or coal gas; it is placed in operation in the winter months.

PRODUCER GAS

The modern producer is a steel vessel of moderate size, as for example 10 feet in diameter and 12 feet in height, brick lined, in which any low-grade fuel may be partly burned, while steam in addition to air is sent into the fire. The operation is continuous; the fuel (for instance, low-grade coal) is dropped into the producer at a constant rate. A mixture of air and steam is served all the time. The made gas passes out continuously, and the ashes are removed constantly by a sweeper in

[5] Chapter 46.
[6] For "liquid purification" *see* previous chapter.

the water seal at the base. Such a producer is shown in Figure 100; it carries a water-cooled, rotating arm which levels the charge and prevents the formation of holes. The shell is stationary. The reactions are essentially the same as those which take place in a water-gas plant, but in producer gas, there is contained all the nitrogen entering with the air for combustion, hence its total combustible constituents are low, and its heat value per unit volume also. Numerous forms of producers are on the market; in some of these, the shell rotates.

FIGURE 100.—The Chapman Gas Producer with stationary shell. (C o u r t e s y of the Cooper-Bessemer Corporation, Mt. Vernon, Ohio.)
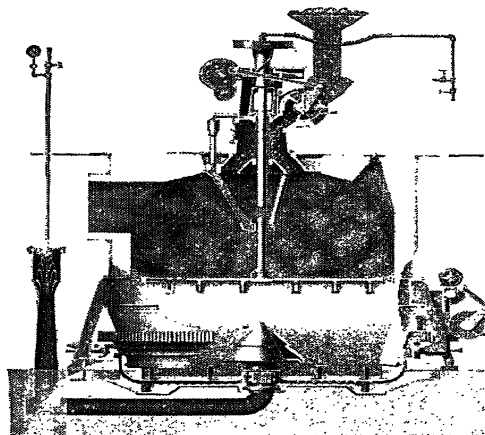
The capacity of a producer 10 feet in diameter and 12 feet high with automatic operation, is 3000 to 4000 pounds of coal per hour. The air-steam mixture is forced in by means of the steam which is applied to an air injector (see illustration); the composition of this mixture is approximately 7 volumes air and 1 of steam. The amount of steam used per pound of coal gasified lies between 0.3 and 0.5 pound, sometimes a little lower, 0.25; the amount depends upon the clinkering properties of the coal used. The volume of gas varies with the grade of coal. The following figures will serve as guides: 1 pound of bituminous coal yields 60 cubic feet; semi-bituminous, 30 cubic feet, and lignite, 28 cubic feet.

NATURAL GAS

Natural gas is found in regions which also have coal or oil, although the wells may be many miles away. Many gas wells do not yield oil, but an oil well almost always produces gas and oil; the gas is then known as casinghead gas. The gas from wells which yield no oil is usually rich in methane and contains some ethane and higher hydrocarbons; its composition remains fairly steady over long periods. The gas obtained with oil (petroleum) is at first methane essentially, but gradually becomes richer in the higher hydrocarbons, and poorer in methane; such gas when

"wet" furnishes a very volatile gasoline, casinghead gasoline, which is largely used to mix with "cracked gasoline" deficient in low-boiling constituents. The methods for extracting gasoline from such gas are compression and cooling methods and absorption by a higher-boiling oil fraction, by charcoal, silica gel, or other absorbent. The value of gasoline extracted from natural gas in 1929 was $158,000,000, in 1935 $54,200,000. The production of gasoline from wet natural gas, for the leading states, expressed in millions of gallons, was in 1935 as follows: California, 527; Texas, 504; Oklahoma, 379; Louisiana, 49; West Virginia, 44; Kansas, 32.

The residual gas after gasoline removal is used as fuel, as is gas from wells [7] yielding no gasoline; but appreciable amounts are burned with an insufficient amount of air for the production of carbon black, or decomposed by heat to form carbon and hydrogen. The development of the natural gas trunk pipe lines has brought about a distribution of this gas which makes it a rival of manufactured gas; as stated before, it is often admixed with coke-oven gas for domestic use. There is a gas trunk line from Amarillo, Texas, to Chicago; another to Indianapolis; in the South and Southeast, a line runs from Shreveport, Louisiana, to Atlanta, Georgia. There are many shorter lines; in 1935 the gas pipe lines totaled over 65,000 miles. No gas pipe lines cross the Rocky Mountains.

The production of natural gas for 1935 (U. S.) was 1,916.6 billions cubic feet, while in 1929 it was 1,917 billions cubic feet..

In the year 1935, the production of natural gas expressed in billions of cubic feet for the several states was: Texas 642, California 284, Oklahoma 275, Louisiana 249, West Virginia 115, Pennsylvania 94, and others less.

The average value of natural gas at the well and unprocessed was 5.8 cents per 1,000 cubic feet in 1935; the residual gas after washing out the gasoline values brings 1 or 2 cents per 1,000 cubic feet. The total number of producing gas wells in 1935 in the United States was 53,790; and of these, 1,401 were drilled and brought in during the year.

Not only in gas form, but in the liquid states is there a large movement of hydrocarbons, of petroleum as well as natural gas origin. In 1935, there were marketed 34.6 million gallons propane, 34.1 million gallons butane, 5.6 million gallons propane-butane mixture, 2.4 million gallons pentane. These liquefied hydrocarbons are shipped in tank cars and tank wagons, in cylinders and drums, and by pipe line. The industrial uses account for 62.3 per cent of the deliveries, domestic (household gas) uses for 27.8, and the rest finds use in the manufacture (or enrichment) of city combustible gas. Some of the industrial uses are given in chapter 24.

Pintsch gas is a compressed oil gas. Blau gas is a mixture of propane, butane, pentane, and hexane containing hydrogen and methane in solution under pressure. The solution is handled in strong steel cylin-

[7] The gas for the chemical laboratory of the University of Buffalo, within the city limits, is furnished by a gas well just outside the building; it is 900 feet deep; the pressure at the well is 200 pounds per square inch. The well has furnished gas under the same pressure for many years past. The amount of gas drawn is moderate.

ders.   Acetylene is presented in Chapter 19.   For isolated laboratories a satisfactory burning gas is obtainable by bubbling air through a low-boiling gasoline; the operation is automatic, a reduction in pressure of the gas causing a water valve to open, whose flow rotates a water turbine which carries the fan.   Another convenient gas for isolated laboratories is "Pyrofax," which is propane, C_3H_8 (boiling point $-42.5°$ C.) compressed in steel cylinders which are transportable.

SURFACE COMBUSTION

Surface combustion is flameless combustion; it takes place when gas with the theoretical amount of air strikes lumps of refractory materials which are at high heat; this material glows, and high temperatures are obtained.   Instead of lumps, a slab or a brick wall may be used.   The advantages of this method of combustion are that the combustion is accelerated, that the energy appears largely as radiant energy which is rapidly transmitted, and that the source of this energy is concentrated. Furnaces have been heated by this method, but of special interest is the operation of a boiler [8] with fire tubes which were filled with refractory fragments on which the combustion took place.   The boiler was 4 feet long, 10 feet in diameter, and without brick setting; the generation of heat took place within the 4-foot fire tubes.   This unusual method of heating promises important economies.

Surface combustion is a catalytic process; the combination of gas and oxygen is accelerated by the contact substance, here fragments of fire-bricks.   It may be applied with water gas, coke-oven gas, natural gas; whether producer gas may be used is not quite settled.

OTHER PATENTS

U. S. Patent 1,880,010, continuous generation of water gas by use of pulverized fuel and steam; 1,855,309, water-gas generator and process for making combustible gas; 1,833,964, process for making water-gas of a high Btu.; 1,829,767, 1,828,461, 1,788,400, and 1,827,169, processes for making carburetted water gas; 1,814,580, process for making producer gas; 2,029,317, gas making apparatus, process for catalytic conversion of hydrocarbon fluids into fuel gas by reacting a hydrocarbon with steam in the presence of a catalyst at high temperature.

PROBLEMS

1. The composition of the several commercial combustible gases in the text are volume percentages.   The heat of combustion for the several constituents in pure form is as follows: Ethylene, 1591 Btu. per cubic foot; carbon monoxide, 322; hydrogen, 329; methane, 1003; ethane, 1755; benzene, 4004 (for low percentages only); disregard the non-combustible gases.   Compute on the basis of the percentage composition and the heat value for the substance, the heat value or heat of combustion for the several mixed gases given in the table; compare with the Btu. value reported there.   There should be close agreement.   These figures are all in terms of the "high Btu." results.   (Figures from Marks' "Engineering Handbook," New York, McGraw-Hill Book Co.)

2. Find the corresponding volumes of typical combustible gases which must be

[8] "Coal and its scientific uses," William A. Bone, who developed this boiler.   London and New York, Longmans, Green and Co., 1918, p. 445, or *Proc. Am. Gas Institute*, **6**, 565 (1911).

burned to fit Problem 1, Chapter 12, in cubic feet at 62° F. and atmospheric pressure.

3. It is necessary to furnish 50,000 cu. ft. of producer gas per hour to a furnace. Using the yield figures given in the text, how many pounds of bituminous coal, semi-bituminous, and lignite will be required per day?

READING REFERENCES

"Coal and its scientific uses," William A. Bone, London and New York, Longmans, Green and Co., 1918.

"Coal carbonization," Horace C. Porter, New York, Chemical Catalog Co., Inc., 1924.

"The recovery of gasoline from natural gas," George A. Burrell, New York, Chemical Catalog Co., Inc., 1925.

"Manufacturing plant of the Providence Gas Company," *Chem. Met. Eng.*, 21, 34, 88 (1919).

"Modern gasworks practice," Alwynne Meade, Ernest Benn, Ltd., London, 1921.

"Natural gas handbook," J. C. Diehl, American Meter Co., Erie, Pa., 1927.

"Handbook of casinghead gas," H. P. Westcott, American Meter Co., Erie, Pa.

"Long distance transportation of natural gas," Edgar G. Hill and George I. Rhodes, *Trans. Am. Inst. Chem. Eng.*, 25, 58 (1930).

"New processes aid in manufacturing clean gas," D. L. Jacobson, *Chem. Met. Eng.*, 36, 58 (1929), includes a description of a waterless gas holder.

A map showing the natural gas trunk pipe lines in the United States may be obtained at a nominal price from the Oil and Gas Journal, Tulsa, Okla.

"Natural gas, its production and distribution," G. R. Hopkins, *Ind. Eng. Chem.*, 22, 502 (1930), with a map of the principal natural gas lines.

"Industrial gases," H. C. Greenwood, London, Balliere, Tyndall, and Cox, 1920.

"Gas calorimetry," C. G. Hyde, London, Ernest Benn, Ltd., 1932.

"The hydrogenation-cracking of creosote for motor fuel," C. M. Cawley, C. C. Hall, J. G. King, *J. Soc. Chem. Ind.*, 54, 58T (1935).

"A thermal study of the process of manufacture of water gas," A. Parker, *J. Soc. Chem. Ind.*, 46, 72T (1927).

The store of coal in the earth was formed many thousands of years ago; when it is exhausted, man will not be able to replace it. It is different from wood, which can be grown within a few years; the scientific exploitation of the forest resources provides for replanting so that new wood grows at about the same rate as older wood is cut. To put the difference in another way: using coal means the exhaustion of capital; using wood means drawing on earnings only.

Chapter 16

The Distillation of Hardwood for Charcoal and By-Products; the Hydrolysis of Wood

The distillation of hardwood for charcoal, with the recovery of the volatile by-products, pyroligneous acid and wood-tar, has taken the place of the old process of making charcoal by the slow burning of a pile of wood covered with earth. The by-product retorts bear the same relation to the charcoal mounds which the by-product coke ovens bear to the beehive coke ovens. On refining the pyroligneous acid there are obtained methyl alcohol or methanol CH_3OH, acetone $CH_3 . CO . CH_3$, acetic acid $CH_3 . COOH$, and a number of less important substances. The tar yields guaiacol $CH_3O . C_6H_4 . OH (1,2)$, solvent oil, and pitch. From the acetic acid, acetic anhydride or acetone may be made. The products are all of importance in chemical technology. Methanol is a good solvent for shellac, other gums, and resins; it is a denaturant, and the raw material for the manufacture of formaldehyde. Acetic acid and acetic anhydride play a major rôle in the manufacture of acetate silk.

Until a few years ago, this industry seemed securely established; since then, three newer developments have threatened it. Acetone is made by a fermentation process, and by a synthetic process. Methanol is produced in large quantities by synthetic means. Acetic acid is manufactured from acetylene. All these processes are described in detail elsewhere in the book. It seems likely that the hardwood distillation industry will continue nevertheless, thanks to domestic and industrial demands for charcoal, and to improvements in the recovery of the by-products.

The industry is of importance in the states of Pennsylvania, New York, Michigan, and Tennessee; charcoal is made in Sweden and Norway, mainly without by-product recovery. Canada has hardwood distilling plants in the provinces of Ontario and Quebec.

Retort with Steel Buggies. In the older practice, 2 cords of air-dried wood (beech, maple, oak, hickory) cut in 4-foot lengths, are piled on a steel buggy; four buggies are pushed into a retort, 55 feet long, which they just fill. The retort is made of steel, with an outer brick shape which leaves a space around the sides and top in which the fire gases circulate. The doors are closed, and heat applied by burning natural gas or oil. Two openings in the rear wall allow the volatile products to pass out.

The cycle is 24 hours; during the first few hours, the heating is rapid, in order to reach the distillation temperature; water comes over first. An exothermic reaction takes place next, when the outside heat must be decreased; the valuable vapors begin to pass out. After about 10 hours, the flames in the burners are raised again, but not as high as at first. After 22 hours, the distillation is over; all burners are turned off, and the retort is allowed to cool for 2 hours.
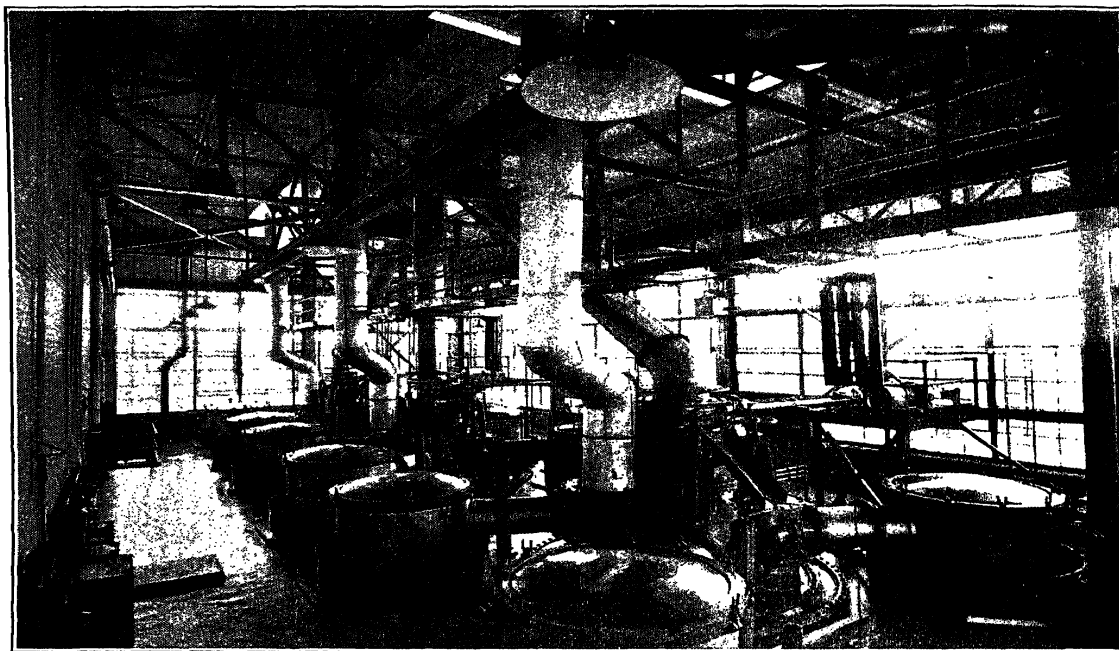
FIGURE 101.—Operating floor of the retort department. The top of the Stafford retorts (3) are flush with the floor; around each retort, four condensers are grouped. Each retort has a feed pipe terminating in a motor-driven barrel valve. The pipe with the offset leading out of each retort is for the fire-gases during preheating period. (Courtesy of the Ford Motor Company, Dearborn, Mich.)

The buggies are placed in air-tight cooling chambers for two days, with a quenching spray of water after the first day. The charge shrinks considerably during the distillation, but the charcoal is obtained in the form of rather large pieces, and very little dust.

A cord of seasoned wood weighs about 3000 lbs.; the charcoal produced is about 1000 lbs., and the amount of permanent gas 7000 to 9000 cubic feet.[1]

Retorts with Continuous Operation. The wood-distillation plant of the Ford Motor Company is a departure from the old practice not only

[1] A table will be found on p. 10 of "Distillation of hardwoods in Canada," by Bates; *see under* reading references.

in the acetic recovery method, but also in the retorts for the distillation. These operate continuously, and still another difference is that the heat comes entirely from the exothermic reaction with which all wood distillers are familiar; a newly cleaned retort must be brought to the proper temperature by burning wood gas, but once the necessary temperature, 540° C. (1004° F.), has been reached, no external heat is needed.

The plant was erected in order to utilize the scrap wood from the automobile body plant; it was desired not to make acetic acid, but ethyl acetate, which the Company requires in its lacquer and artificial leather departments. (*See* Fig. 101.)

Flow Sheet for the Ford Continuous Wood Distillation Plant, Iron Mountain, Mich.

Hogged scrap wood (4 to 10% moisture) → Rotary wood driers 10 feet by 100 feet long
↓
Stafford retorts 10 feet by 40 feet
↓
Wood gas | Pyroligneous acid | Tar | Charcoal
Pyroligneous acid ↓ Primary still
Tar | Oil | Pitch
Charcoal ↓ Coolers ↓ Conditioner ↓ Screens and briquetting machine
Acid distillate | Tar Creosote
Acid distillate ↓ Continuous still
Overhead 95% methanol refined further | Base 15% acetic acid
Base 15% acetic acid ↓ Ethyl acetate plant

The operation may be described as follows:[2] The scrap wood is reduced to small size (up to 8 inches by 2 inches by $\frac{3}{4}$ inch) in a hog mill, passed through a drier reducing moisture to 0.5%, and fed through barrel valves [3] at the top of the Badger-Stafford retorts. These are vertical cylinders of steel, 10 feet wide by 40 feet high, with a heat-insulating inside wall 18 inches thick, composed of fire-brick, diatomaceous earth, and insulating brick. The heat developed by the exothermic reaction near the center of the retort rises with the vapors and gases developed, and warms the incoming charge until it reaches the reaction temperature and itself distills. The average temperature in the center of the retort is 515° C. (950° F.) and near the bottom, 255° C. (490° F.). The carbonized material is discharged at the bottom through a barrel valve (Fig. 102). The charcoal drops into a cooler 6 feet in diameter and 30 feet long, cooled by water

[2] From a description kindly furnished by the Ford Motor Company.

[3] A barrel valve may be said to consist of two barrels, one fitting inside the other, and the inner one free to rotate by turning its axis; the inner barrel has two staves missing, so that the charge falls inside of it. By turning, the charge is dumped, while the vessel at the same time is sealed.

coils and a trickle of water on the outside. It passes next to the rotary conditioner, where it absorbs oxygen; the heat of absorption is dissipated by cooling water over the outer walls. It is now ready for screening and briquetting. It takes 5 hours for the conditioning, instead of 48 hours in the standard buggy coolers.

The gases and vapors passing out of the retort are cooled, the condensed pyroligneous acid is stored, the gas is scrubbed and blown to the power house and burned under boilers, except the part which is used to bring a fresh retort up to the proper temperature.
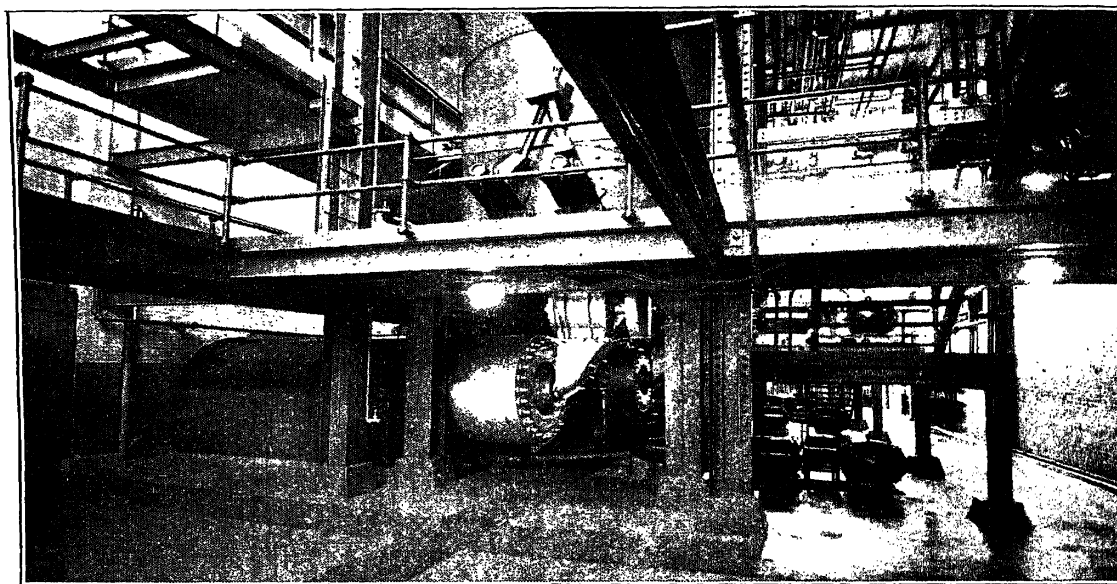
Figure 102.—First floor of retort department, showing the bottom and charcoal discharge end of the Stafford retort. The bars for shaking the grates are visible in upper center. The motor-driven barrel valve conveys the charcoal to the cooler, which extends beyond the wall to the left. The head of the second cooler is visible. (*Courtesy of the Ford Motor Company, Dearborn, Mich.*)

After operating two weeks, a retort must be taken off the line, and the accumulated tar burned out; it is then brought up to temperature by burning wood gas in it for 24 hours.

The pyroligneous acid is settled and distilled from batch primary stills to remove dissolved tar. The acid distillate then goes to a continuous still, which gives overhead 95 per cent methanol, and at the base 15 per cent acetic acid.

The methanol is refined in two discontinuous stills, whose several "cuts" are refined further to give 75 per cent methyl acetone, 75 per cent methyl acetate, and C. P. methanol.

The 15 per cent acetic acid is treated with ethyl alcohol in the presence of sulfuric acid, to give a crude ethyl acetate; this is treated with

calcium chloride, giving finally dry, pure ethyl acetate. The average yield of the various products is given in Table 29.

The wood used is 70 per cent maple, 25 per cent birch, and 5 per cent ash, elm and oak. The plant is designed for a capacity per day of 400 tons of scrap wood.

TABLE 29.—*Average Yield of Various Products at the Iron Mountain Plant, Ford Motor Company, per Ton of Dry Wood, 1936.*

Charcoal	649 pounds
Gas	5000 cubic feet
C. P. methanol	3.66 gallons
Methyl acetone (and *Methyl Acetate*)	1.46 gallons
Allyl alcohol	.05 gallon
Ketones	.30 gallon
Methyl acetate	0.945 gallon
Soluble tar	37.46 gallons
Pitch	66.9 pounds
Creosote oil	3.25 gallons
Ethyl acetate	11.65 gallons
Ethyl formate	1.27 gallons

The average composition of the gas from the Badger-Stafford retorts is hydrogen 2.2 per cent by volume, dry gas; methane 16.8; C_nH_m 1.2; carbon monoxide 23.4; carbon dioxide 37.9; oxygen 2.4; nitrogen 16.0; Btu. per cubic foot 290.

DIRECT RECOVERY OF ACETIC ACID

In the early days, the plant in the mountains made its acetic acid transportable by changing it into calcium acetate, which involved neutralization with lime, and evaporating to dryness. The customer had to distill this acetate with sulfuric acid in order to obtain the free acid. The development of synthetic acetic acid made it economically impossible to continue this procedure; the wood distillation plants were the more pressed to reduce costs, in that synthetic methanol had cut the price of their second product, wood alcohol. Three processes have been invented and perfected by the users, in which the acetic acid is extracted from the acid distillate by means of solvents, with subsequent separation by distillation. The Brewster process uses isopropyl ether as the solvent; the Suida process uses a high-boiling wood oil fraction, produced from the wood in the plant, and used over and over again for a reasonable number of cycles. The expense of buying a dissolving agent thus disappears in the Suida process, and an acetic acid of 92 per cent strength is produced, of high purity. A third process is the Othmer process. When it is added that in some states there is a steady market for charcoal for domestic use, it will be seen that, most happily, this interesting industry has a new lease on life. The Brewster process, it might be added, is particularly applicable to the recovery of acetic acid in a cellulose acetate plant.

The Suida Process.[4] The apparatus, aside from retorts and the copper condensing equipment, includes a primary boiler, a scrubbing column, a dehydrating column, the second boiler, a stripping column (10 plates), a rectifying column (30 plates), a still for tar, and one for pitch, both with condensers and receivers. (See Fig. 103.)

FIGURE 103.—Flow sheet of the Suida process for the extraction of acetic acid directly from the pyroligneous acid vapors. (Courtesy of Forest Products Chemical Company, Memphis, Tenn.)

The extraction is carried out in the superheated vapor phase. The settled pyroligneous acid is run to the primary still, which sends out vapors of acetic acid, alcohol, and water, retaining the dissolved tar, which is run off periodically. The heating is by closed steam coils, and the vessel and coils are of copper.

The vapors of acetic acid, crude methanol, and water enter at the base of a plate column, called the scrubbing column. (*See* Fig. 104.) Solvent oil enters near the top of the column and flows downward, while the vapors pass upward. The solvent oil takes up acetic acid vapors and some water. There is drawn from the base of the tower, solvent oil charged with acetic acid and some water; there passes out of the column at the top crude methyl alcohol, aldehydes, and water. This overhead distillate is condensed and, for the most part, run to the weak alcohol storage; a small amount is returned to the still as reflux. The oil with acetic acid passes down the dehydrating tower, and from there to the sec-

4 "Acetic acid and cellulose acetate in the United States," E. P. Partridge, *Ind. Eng. Chem.*, 23, 482 (1931); "Suida process for acetic acid recovery," E. P. Poste, *Ind. Eng. Chem.*, 24, 722 (1932).

ond boiler (not shown on flow sheet) ; which delivers the heated liquid to the stripping tower, operated under vacuum. Here the acetic acid vapors are flashed off (that is, vaporized with explosive violence) and enter the rectifying column, carrying a small amount of oil with them and all the water present. The lower part of the stripping column serves to exhaust the oil of acetic acid. In the rectifying column, the oil is retained on the first few plates, and acetic acid of 92 per cent CH_3COOH is drawn off as product from the twelfth plate from the bottom. The upper 18 plates receive most of the water which entered the rectifying tower; they carry an acetic acid solution which becomes gradually weaker. There passes out at the top a 15 per cent acetic acid which is condensed and returned, mainly, to the pyroligneous storage.

The solvent oil leaves the stripping tower free from acid; it is cooled and returned to the scrubbing tower. It is obtained in the first place as follows: the tar is distilled and the distillate gives a light oil, and a
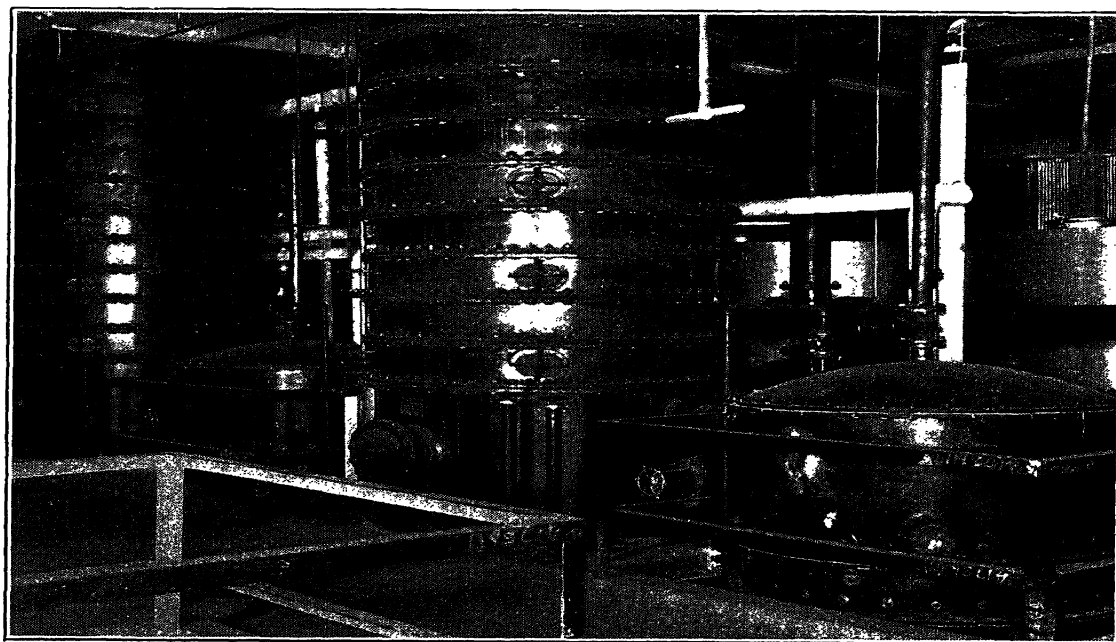
FIGURE 104.—The Suida process. Scrubbing columns, with the tops of the dehydrating columns shown. (Courtesy of Mr. T. C. Albin, Forest Products Chemical Co., Memphis, Tenn.)

heavy oil fraction. The latter is placed in the tar still, and distilled again. The distillate is divided into light oil, heavy oil, and scrubbing oil; it is the last fraction which serves as solvent. The excess is sold or burned as fuel.

In the *Othmer process* [4a] for direct acetic acid, a "withdrawing agent" such as ethylene chloride, or butyl alcohol, is added; there distills over an azeotropic mixture, with water one of its components. On cooling the vapors, the "withdrawing agent" forms a separate layer so that it is readily recovered and used over again. The acetic acid, free from water, is left in the bottom of the still.

Several additional observations are in order. As modified in the American practice, the methanol need not be removed in a preliminary distillation of the pyroligneous acid; distilling the alcohol simultaneously with the removal of acetic acid by the solvent reduces by half the amount of esters formed; to that extent the alcohol as such is preserved, also the acid. A plant which finds the production of calcium acetate no longer profitable can be changed into a Suida plant, using the same retorts. Pure acetone formerly was made exclusively by the distillation of calcium acetate; it is now obtained by fermentation or by synthesis.

As to future trends, "both the wood distiller and the producer of synthetic acetic acid from acetylene are open to the danger of competition from newer and cheaper synthetic processes. One of the possibilities is the oxidation of ethanol to acetic acid. The ethanol may be derived from fermentation, or be made by synthesis from ethylene." [5] This latter development would be due in great part to the loss of the regular market for ethanol, displaced by the cheaper synthetic methanol.

There were produced in 1935 34,157,752 bushels of charcoal, 4,528,480 gallons of crude methanol, 25,846 tons of acetate of lime, directly recovered acetic and some esters to the value of $1,889,796, tar 10 million gallons, tar oils 1,087,492 gallons. The total value for all wood distillation products including turpentine and rosin was $15,757,391.

Refining the Alcohol. The crude alcohol fraction is separated into a number of purer substances in a continuous distillation with plate towers, similar to the procedure used for ethyl alcohol, fully described in Chapter 20. In a crude containing 82 per cent organic substances, there are 6 to 8 per cent methyl acetate $CH_3 . COOCH_3$, 12 to 14 per cent acetone, 65 per cent methanol, and not over 1 per cent other organic bodies such as allyl alcohol $CH_2 : CH . CH_2OH$, methyl ethyl ketone $CH_3 . CO . C_2H_5$. The separation is mainly in four grades: acetaldehyde boiling at 20° C. (68° F.); acetone with 28 per cent methyl acetate, 51 per cent acetone, and 21 per cent hydrous methanol, used as an excellent solvent for nitrocellulose under the name of "methyl acetone" [6]; a high test methanol, and the allyl compounds.

Acetaldehyde may be transformed into paraldehyde, a polymer $(CH_3 . CHO)_2$, by the action of a small amount of concentrated sulfuric acid. Paraldehyde is a liquid boiling at 128° C. (262° F.); it is a valuable hypnotic.

[4a] U. S. Patents 1,804,745 and 1,917,391. *See* further: "Dehydrating aqueous solutions of acetic acid." *Donald F. Othmer, Chem. Met. Eng.*, **40**, 631 (1933); and **41**, 81 (1934).

[5] *Ind. Eng. Chem.*, E. P. Partridge, **23**, 488 (1931).

[6] Acetone is not isolated as such from crude wood spirits; methyl acetate and acetone form a constant boiling mixture.

Acetone from Calcium Acetate. Acetone is made by fermentation of starch, with butyl alcohol as a second product (Chapter 20), but the old method might be mentioned, for, in an emergency, it could be revived. Dilute acetic acid is treated with lime, to form a solution of calcium acetate, which is concentrated to dryness; the solid is then heated, when it breaks down to form acetone and calcium carbonate. After the heating, steam is blown into the vessel in order to drive out all the acetone. The boiling point of acetone is 56° C. (133° F.).

$$2CH_3 . COOH + CaO = (CH_3 . COO)_2Ca + H_2O ;$$
acetic acid

$$(CH_3 . COO)_2Ca = CH_3 . CO . CH_3 + CaCO_3$$
calcium acetate   acetone
(a solid)
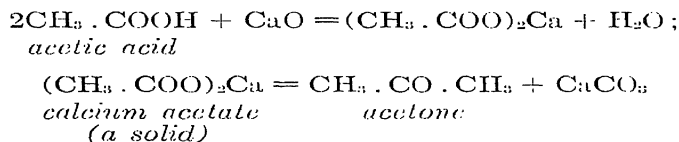
Acetic Anhydride. A portion of the acetic acid production is used to make sodium acetate, and this in turn serves as raw material for the manufacture of acetic anhydride. The method consists of mixing sodium acetate with sulfur chloride (SCl_2) and passing in chlorine, maintaining a temperature of 15° to 20° C. by cooling coils[7]; after the reaction is complete, the reaction mixture is heated two hours to 80° C., and then the acetic anhydride distilled. The latter boils at 138° C. (glacial acetic acid boils at 119° C.), and is best distilled at reduced pressure. The reaction is:

$$8CH_3COONa + SCl_2 + 2Cl_2 = 4(CH_3CO)_2O + 6NaCl + Na_2SO_4.$$
acetic
anhydride
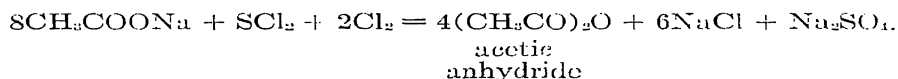
In other patent proposals, successfully demonstrated, the sulfur chloride and sodium acetate are mixed with acetic anhydride, and then chlorine gas passed in.

Acetic anhydride has a penetrating, painful odor. It is used in the manufacture of cellulose acetate, in the dye industry, and in the preparation of certain pharmaceuticals.

BERGIUS PROCESS FOR WOOD HYDROLYSIS

The conversion of wood cellulose to sugars suitable for animal and human consumption by hydrolyzing it with hydrochloric acid in the cold on the commercial scale is an accomplished fact. The world is indebted for this contribution to the genius and persistence of Dr. Friedrich Bergius.

On treating the chipped wood[8] with 40 per cent hydrochloric acid at 20° C. [68° F.] in a bank of extractors or diffusers, there is produced a liquid, the hydrolysate, and a brown solid residue, the lignin. The hydrolysate is distilled in order to remove and recover the hydrochloric acid, and the acetic acid which pass out at the same stage; the two are

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[7] German Patent 273,101, an improvement on 222,236, 241,898, and 132,605.
[8] The wood studied has been pine, in one extended run, and beech, in another.

separated. The concentrated residue is dried and is then the raw sugar, with some residual acid. The lignin retains the skeleton form of the wood chip; for the present it is made into briquets, but better uses are in process of development.
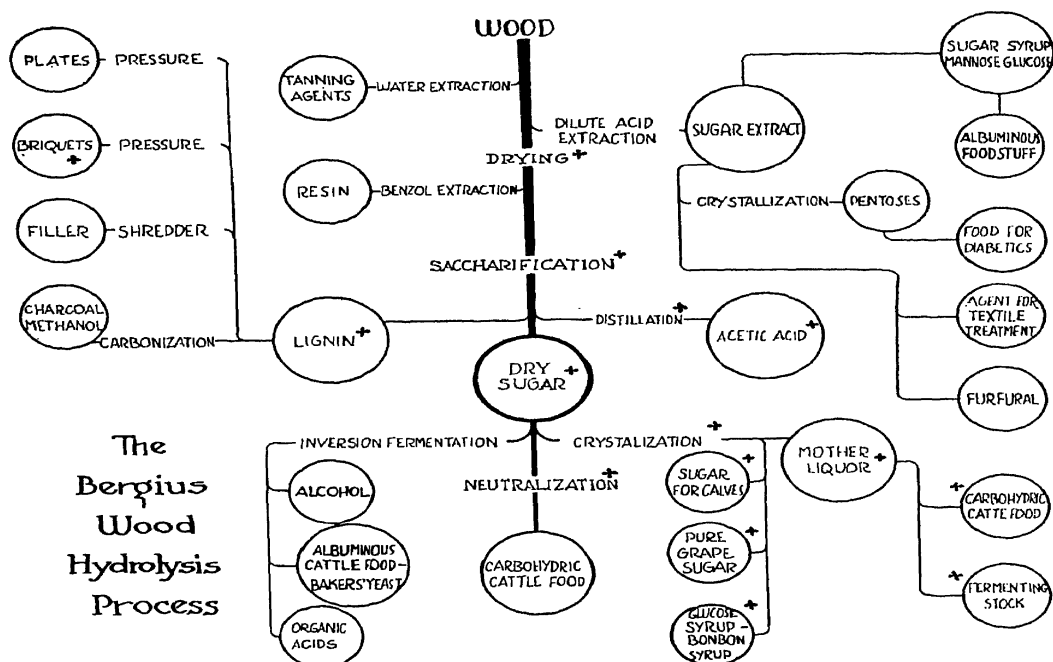
FIGURE 105.—The complete products-diagram for the Bergius wood hydrolysis process, not fully realized in the present practice (1936). The steps and products actually on a factory scale are designated with an asterisk (by ERR). The inversion-fermentation is an alternate to the sugar production. The water, dilute acid, and benzene extractions must proceed saccharification. Based on the original German sketch kindly supplied by Dr. Friedrich Bergius.

The raw sugar after a lime treatment is an acceptable cattle food. Its tetrameric sugar molecules may be inverted to give the glucose, and may be the basis of a glucose syrup, or after further purification and decolorization, will produce crystal glucose. If preferred, the sugars may be fermented to give ethyl alcohol; in this case, about 80 per cent of the sugar (glucose) ferments, but the residue, xylose and galactose, are best worked up into cattle feed.

An annual production of 6,000 metric tons of raw sugar was expected for 1936.

A number of further details will be gleaned from the accompanying flow-sheet and product diagram. Numerous questions as to the choice of material for construction had to be solved.[9]

[9] For picture of Haveg tanks used, *see* Chapter 45.

It should be noted that this process recovers as sugars the same matter which in the ordinary wood distillation goes out as carbon dioxide and water. The same values in acetic acid, alcohol, lignin are obtainable besides, and in spite of the hydrolysis. Also, waste wood, not otherwise utilized at all, may be the raw material.

TURPENTINE AND ROSIN

Pure gum turpentine is obtained by distilling the sap of the Southern pine. Wood turpentine is a similar product; it is obtained by distilling the wood, usually stumps and small branches, rather than the trunk which serves for lumber. The States most prominent in both industries are Florida, Georgia, Alabama, and Louisiana. The Scandinavian Peninsula produces turpentine from the Norway pine.

For the gum turpentine, incisions are made in the trunk of the pine, leading into a cup which can hold one-half to 1 gallon of sap; the sap flows from March to September. The collected sap is distilled from a copper still; turpentine and water pass over, and there is left in the still the rosin. In some plants, steam is passed in from the beginning, in others it is introduced after the turpentine and water distillate stops,
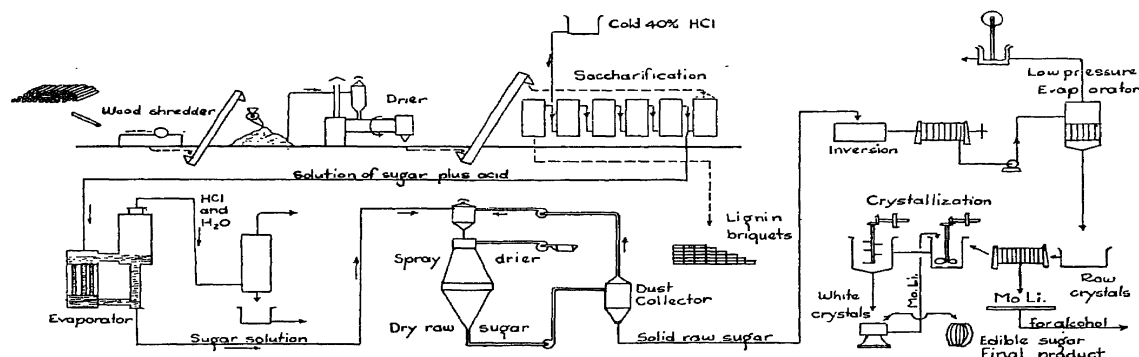
FIGURE 106.—Diagrammatic flow sheet for the Bergius wood hydrolysis process.

giving an additional amount. About 20 per cent of the sap is recovered as turpentine. Its uses are based mainly on its solvent properties in paints; its high content of pinene permits the manufacture of pinene hydrochloride, a solid, and other chemical substances.

Wood turpentine is obtained by the dry distillation of the wood, with or without the introduction of steam. The process is very similar to hardwood distillation, but horizontal retorts of smaller size in which the wood or chips are placed without buggies are common. Wood turpentine differs from gum turpentine in its odor.

For the year 1935, the production in the United States was as follows (from the Bureau of the Census figures):

Turpentine, distilled from wood .... 4,611,641 gallons
Pine oil .... 3,443,315 gallons
Rosin, from wood .... 529,001 barrels
Turpentine from crude gum .... 24,850,000 gallons
Rosin from crude gum .... 1,647,000 barrels

(The barrel equals 500 pounds)

Some of the uses of rosin are given in Chapters 31 and 35.

OTHER PATENTS

U. S. Patent 1,792,392, on turpentine, pine oil and rosin from wood rich in oleoresin by the direct action of strong current of steam to volatilize the oils; 1,772,895, turpentine substitute from pine oil, by adding fuller's earth to pine oil and distilling with steam at a temperature of 125° to 225° C.; 1,740,115, extraction of turpentine pine oil and rosin from resinous woods, by solvents; 1,859,292, thermal decomposition of wood by subjecting it to direct physical contact and reaction with a highly heated body of hydrocarbons; 1,836,305, wood distillation apparatus; 1,731,242, method of wood distillation; 2,050,235, concentrating acetic acid; 2,034,332, concentrating aqueous formic acid.

PROBLEMS

1. A plant using retorts with steel buggies distills 30 cords of beech wood for 100 days. What is the total tonnage of charcoal, and how much gas is available per day?

2. A plant distills every day 200 tons of chipped waste hardwood in continuous retorts. Consulting the table of products given in text, what are the amounts of each which are obtained? Make an allowance for the gas required for cleaning the retorts and bringing them up to heat.

3. A chipped pine wood contains for each 100 kilograms of dried wood 66 kilograms of reducing sugars, with the composition:

	Per cent
Glucose	60
Mannose	17-21
Galactose	5
Xylose	13
Fructose	1

Allowing the glucose and fructose to ferment without loss to ethyl alcohol, how much of this substance, on the 100 per cent basis, will be obtained?

The same pine chips give per 100 kilograms 2 to 2½ kilograms acetic acid, and 33 kilograms of lignin.

4. A chipped beech wood produces for each 100 kilograms of dried wood 72 kilograms of reducing sugars, with the composition:

	Per cent
Glucose	67
Xylose	28
Other sugars	5

and 25 kilograms lignin, and 6 kilograms acetic acid.

Let the glucose be worked up into a 50 per cent glucose syrup, how much will be obtained per 100 kilograms of wood? Let the remaining sugars be made into cattle feed, what is the weight they will contribute, assuming none is lost? With the acetic production as given, how many pounds of acetic acid would be obtained from one cord of this same wood? (the weight of wood per cord given in the chapter text may be taken as applying).

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"Pine stumps to fine chemicals," R. C. Palmer, *The du Pont Magazine,* 31, No. 4. 18 (1937).

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"Sugar from wood," W. R. Ormandy, *J. Soc. Chem. Ind. (Brit.),* 45, 267T (1926), describing the Rheinau, the Prodor, the combined process, and the Classen process

The electric furnace is a comparatively modern device; until its advent, the highest temperature commercially available was the white heat of a bed of coal burning under forced draft, which gives about 1400° C. In the electric furnace, a temperature three times as high is obtainable, about 4100° C.; this is not so very far from the estimated temperature of the sun's surface, 6200° C. That the high temperature of the electric furnace should have made possible the manufacture of products hitherto unknown, or known only in the natural state, is not surprising. Important among these are artificial graphite, silicon carbide, aluminum oxide, calcium carbide, and certain alloys.

Chapter 17

Products of the Electrothermal Furnace

There are three main types of electric furnaces, the arc furnace, the resistance furnace, and the induction furnace. In the arc furnace, the heat of the arc is utilized, with perhaps an electrical effect in the case of gases. In the resistance furnace, no arc is formed, but the electrical energy is entirely transformed into heat or thermal energy. If the material furnishing the resistance is the charge itself, the resistance furnace is said to have direct heating. If a material is added purposely for the sake of the resistance it furnishes, without being part of the reacting charge, the furnace is said to have indirect heating. The induction furnace may be applied only to metals; it is based upon this fact, that if an alternating current of high frequency is passed through a coil of many turns (primary) in the center of which a soft iron core is situated, an alternating magnetic field is formed, and a single iron ring (secondary) placed around the first coil and core will become red hot in a few minutes. In addition to these three types, some furnaces involve a combination of two types. Any of these furnaces may be termed electrothermal, for their value lies in the heat they furnish, and that heat has its source in electrical energy. The materials produced in the electrothermal furnace could not be made by means of heat from any other source; it is the high degree of heat which is essential. At the present time no other means for the production of such high temperatures is known. The size of the furnace does not matter; a small furnace a few inches in size is as truly an electric furnace as the large furnace for graphite, 30 feet long.

ARTIFICIAL GRAPHITE

Artificial graphite is made in an electrothermal furnace with direct heating. When coke is heated to the very high temperature which this furnace affords, a change takes place, at the end of which the ash is volatilized as well as any other ordinarily more volatile impurities, and there is left only carbon in the form of graphite. The content of the ash functions as the graphitizing agent; it forms carbides with the coke; later the carbides decompose, and the carbon is left in the form of graphite.

The heating must be done in the absence of air; this is accomplished by covering the heated material with a sand mixture.

Certain materials are added to the coke in order to produce shaped pieces, for example, electrodes for electric furnaces and for electrolytic cells; it is these electrodes particularly which have made this industry an indispensable one. Graphite is a good conductor of electricity, coke is a poor one.

ELECTRODES FOR ELECTRIC FURNACES

The raw materials for artificial graphite are: calcined petroleum coke, the residue from the distillation of certain crude oils for gasoline; coal-tar pitch, and a petroleum distillate called black-summer oil. A portion of the coke is powdered in a Raymond mill to such fineness that 60 per cent passes through a 200-mesh screen [1]; another portion of the coke is crushed
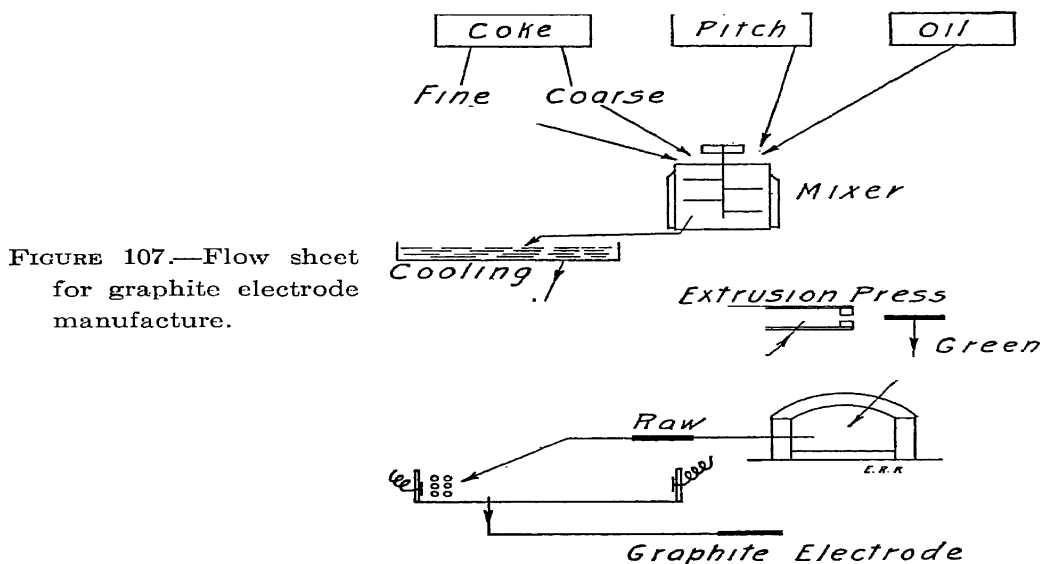
FIGURE 107.—Flow sheet for graphite electrode manufacture.

in a swing-hammer mill to a coarse powder. These two sizes are mixed with pitch and oil in steam-jacketed mixers for a period varying from 20 minutes to an hour.[2] The charge is dumped onto the floor and allowed to cool to 95° C. (203° F.) ; it is then shoveled to a chute feeding a cylindrical form open at both ends, and placed on a movable table, so that the form may be brought under a ram which presses the soft mass into a cake 16 inches in diameter and 10 inches high, weighing 60 to 70 pounds. The cakes are fed at intervals to an extrusion press, enough cakes being used to fill it. This press is merely a steam-jacketed cylinder of 17-inch

[1] Chapter 44.
[2] The different sizes of coke are used in order to obtain minimum voids.

internal bore, fitted at one end with a steam-heated die which may be changed to suit the order; at the other end with a piston hydraulically driven. The mass is extruded through the die, very slowly, onto a receiving plate. The diameter of the electrode is fixed by the die opening; the length is measured on a stick, and cut off with a wire, as cheese would be. Two men operate the extrusion end of the press; one operates the valves.

The pieces, now called the "green" electrodes, are lowered to the floor and rolled away in shallow troughs with 2 inches of water, and under a spray of cold water. By reason of this cooling, the soft mass becomes comparatively stiff; the green electrodes are now ready for firing. The amount of compression is reflected in the specific gravity: the 16-inch cake has a specific gravity of 1.3; the green electrode, 1.7.

First Baking, producing Raw Electrodes. A first baking is done at a temperature of not over 1100° C. (2012° F.), producing a hard substance with a metallic ring. This may be done in the electric furnace, and may be followed without repacking by the graphitizing heat, merely by changing from a low transformer to a high one; but it is found more economical to perform the first baking in coal-fired kilns with removable arches. The kilns are of such size that for electrodes 4 inches in diameter (circular) and 40 inches long, 500 may be baked at one time in one kiln. The electrodes are packed in sand, preferably re-used sand, so that they do not touch each other, and are well covered so that the fire gases which pass over the top will not come in contact with them. The fire gases pass over the charge, down the sides and rear, and under the floor of the kiln by means of suitable channels and cross walls in the brickwork, before they can escape to the stack. A pyrometer [3] reaches into the sand, another is placed in the fire gases. The temperature is raised slowly, 5° C. per hour, requiring 5 to 7 days; when 800° C. (1472° F.) is reached, all danger of forming blow-holes is over and the fire is forced until the pyrometer in the sand registers 1100° C. (2012° F.); this heat is maintained for 2 to 3 days.

The charge is cooled slowly; first the arch is removed by an overhead traveling crane; after a day, some of the sand blanket is removed; some more on subsequent days, finally all. The cold charge is unpacked, and the raw electrodes are ready for the graphitizing heat. The gradual cooling is necessary as the electrodes would take fire if air could reach them while still hot.

During the baking, there is a loss in weight of 13 per cent and a shrinkage in length of 1 per cent. The green electrode, 4 by 40 inches, weighs 29 pounds.

Graphitizing the Raw Electrodes. The raw electrodes are changed from a hard body to one so soft that it may be cut with a pocket knife, in an electric furnace in which the charge itself forms the resistance to the electric current. The heat attained in the furnace is about 4100° C. (7366° F.), whereas the maximum heat which the coal-fired kiln affords

[3] Chapter 46.

is 1400° C. (2552° F.). The furnace consists of a bed of concrete flags supported on short piers placed close together, and of two upright end pieces also of concrete. The length is 30 feet, from upright to upright; the width is 13 feet; there are no stationary side walls. When fully charged the height of the bed is about 6 feet.

The end pieces are provided with openings to receive the stationary graphite blocks forming the terminal electrodes for the furnace; each end piece has eight carbon blocks, 6 inches square, in cross-section, long enough to protrude 2 inches within the furnace and to extend 6 inches outside for connection to the copper leads. The connection to the graphite terminals is kept cold by a stream of water.

FIGURE 108.—Plan and elevation of artificial graphite furnace for electrodes.
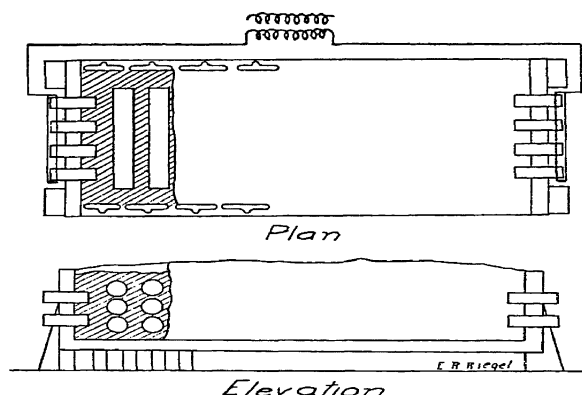
The charge of raw electrodes is packed between the end pieces after placing ground coke over the floor of the furnace to a height of 4 inches; the electrodes are placed crosswise to the long axis of the furnace. They are piled exactly over each other, touching, and the vertical rows are separated by strips of wood, replaced by ground coke when the packing is completed. The total weight of the charge is 30,000 to 35,000 pounds. Along the two sides a layer of coke 3 inches thick is placed reaching from one upright end piece to the other; it is held in place temporarily by a sheet steel apron. A layer of coke is similarly placed over the top. It is through these layers that the current passes at the start, for the raw electrodes are poorer conductors than the coke. The graphite terminals in the end walls are buried in the crushed coke and through it make contact with the electrodes nearest them.

Over the top a layer of mixed sand, coke, and sawdust is spread, to act as a heat-retaining cover; sand previously used, partly converted to silicon carbide, is preferred to new sand. Along the sides concrete blocks 4 feet high are set up at a distance of 12 inches from the 3-inch coke layer, and the space so formed is filled with used sand. The electrodes are now buried in crushed coke and protected from the air on all sides; the furnace is ready for the heat.

The current at Niagara Falls is 25-cycle [4] alternating current; the voltage at the beginning is 240 volts; as the heating progresses the charge becomes more conductive, and the voltage may be dropped gradually; at the end it is 30 volts. The electrical load is 1600 kilowatts at the start; at the end, 1200 kilowatts; this latter load is in the form of 40,000 amperes at 30 volts. The current from the hydroelectric power plants is delivered as 12,000-volt current and transformed to the lower voltage in oil transformers; it is brought to the graphite block terminals by means of eight copper bars 4 inches wide and three-eighth of an inch thick.

As the heating progresses gas escapes from the charge and burns. Pyrometers are used for the first few days; then they are removed as they themselves would be volatilized. The final graphitizing current is on the furnace for two or three days. After the current is shut off, the furnace is allowed to cool for six days (for the largest pieces); it is then unloaded. The complete cycle from one unloading to the next is one month for each furnace.

Graphite electrodes may be machined (threaded, for instance) so that when worn short, the butt ends may be screwed onto the next new piece and thus utilized. Electrodes of all kinds are made, of square and rectangular cross-section as well as circular.

Graphite powder is made by filling the furnace with coarsely powdered coke with a central core of 2-inch square graphite rodding, then proceeding as before. Such "bulk graphite" is powdered in a special mill and finds application in the electroplating industry, in dry batteries or cells,[5] and in lubrication. Mixed with grease it becomes a special lubricant.[6]

Certain articles are baked only a short time, and are semi-graphitized; for example, electric motor brushes.

Artificial graphite is artificial only in the sense that it is manufactured and not that found in nature; it is a purer and more uniform graphite than the natural material. Its higher purity makes it a better conductor and a superior lubricator. For all uses except the manufacture of clay-graphite crucibles, the manufactured graphite excels the natural graphite. The superiority of the latter in making graphite crucibles is due to the presence of mica fragments which prevent the rapid burning which manufactured graphite would permit; these mica pieces furthermore offer points of attachment for the clay binder.

ABRASIVES

Silicon Carbide. In the same kind of electric furnace in which graphite, the softest solid known, is produced, silicon carbide, practically as hard as diamond (the hardest substance known) is also produced;

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[4] 25 cycles per second.

[5] A dry cell consists of a central "raw" carbon rod surrounded by a mix of graphite and manganese dioxide as depolarizers; these are contained in a paper bag, which sets in a mix of starch paste, ammonium chloride, and zinc chloride, surrounded by a zinc cylinder which forms the second pole; the carbon rod is the positive pole.

[6] It is discussed under lubricants, Chapter 24.

but while in the graphite furnace the heat-producing resistance is that of the charge itself, in the silicon carbide furnace a central core of carbon furnishes the needed resistance, and the materials which are to be transformed are heaped around it. Hence the silicon carbide furnace belongs to the class of resistance furnaces with indirect heating. It is important to note that the temperature of the graphite furnace is much higher than the decomposition temperature of silicon carbide, so that none of the hard substance can exist in the soft graphite.

Silicon carbide, or silicide of carbon, SiC, was unknown before the development of the electric furnace.[7] Its great value lies in its hardness, and in its property of breaking off to form fresh sharp surfaces. These two properties have led to its use as an abrasive. It is used in the form of grinding wheels, grinding powders, and polishing papers.

FIGURE 109.—Cross-section of the silicon carbide furnace, showing the central graphite rod surrounded by the core of coke (in blank) and around this the mixed materials forming the charge proper.
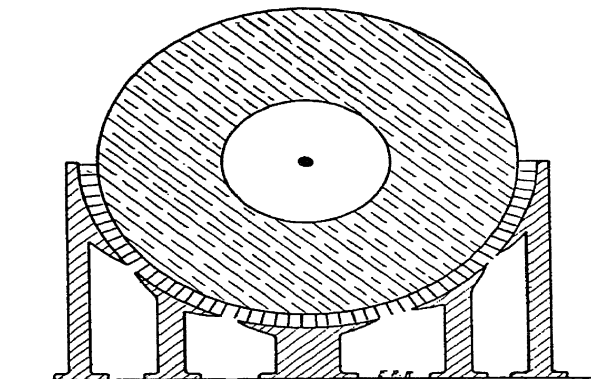
Silicon carbide is sold under the trade names of "Carborundum," "Crystolon," and others.

Silicon carbide is made in furnaces 40 feet long, 7 feet wide and 6 feet high. The charge itself and the heating core form the greater part of the furnace; the permanent portion is only the bed and the two upright end walls in which the electrodes are imbedded. The bed of the furnace consists of curved cast-iron pieces lined with hard fire-bricks, on which the charge rests. The materials for the charge are made up in the proportions of 100 parts of the finest grade glass sand, 60 parts of coke, and 10 parts of sawdust (all by weight). These ingredients are thoroughly mixed and loaded from a bucket carried on an overhead crane; the bucket is filled from a bin on an upper floor, by gravity.

The manner of loading the furnace is as follows: Enough material is charged to reach half-way of the height of the total load; a long furrow 2 to 3 feet wide running from one end wall to the other is then made in the center of the charge, filled with crushed coke, and a 2-inch graphite rod [8] reaching the whole length of the furnace is laid in the middle. The

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[7] The experimental work was done at Monongahela City, Pa., by E. C. Acheson.
[8] Made in the same way and from the same mass as the graphite electrodes.

core widens at the end walls so that all the graphite terminals are in contact with the coke which then runs without a break to the opposite wall. Next enough coke is added to complete the core, and then the remainder of the mixed charge. The furnace is then ready for the current. A portion of the charge remains unchanged and forms the blanket required to keep out the air and to conserve the heat.

The electrical load is 1500 kilowatts, and is continued until a total of 54,000 kilowatt hours have been applied. The current is alternating (25 cycles at Niagara Falls); the voltage is 300 volts at first, 200 volts at the end. The period of heating is about 36 hours, and the maximum temperature 2600° C. (4624° F.) in the reacting mass.[9] Blue flames are visible all over the mass for the greater part of the heating; they consist of carbon monoxide, escaping and burning. Toward the end, these flames turn yellow, as the sodium compounds begin to volatilize and pass out. The furnace is allowed to cool and is then opened. The inner part of the mixed charge is found transformed into large hard chunks consisting of glistening, well-formed, flat crystals of various colors; some regions have a soft velvety violet color, others are green-bronze to light green, others again are colorless. The color cannot be foretold nor regulated; for the manufacturer this is of no importance and perhaps of no interest, but to the visitor a newly opened furnace is a beautiful sight. The crystals are hard, with sharp edges, forming jagged peaks which jut out from the mass.

The desired product forms the inner part of the mixed charge, adjacent to the carbon core, so that moving from the edge inward, there is met first unchanged charge, the silicon carbide crystal layer; next some graphite having the shape of the silicide crystals, because the crystals first formed lost their silicon by overheat; finally the inner core, now partly graphite. From 64,000 pounds of mixed charge, about 16,000 pounds of silicon carbide crystals are obtained. The graphite in the center is a by-product; most of it is sold to electrode makers. The cycle from unloading to unloading is one week.

The function of the sawdust is to make the mass porous so that gases may pass out. It will be noted that enough coke is added to remove the oxygen from the sand in addition to the amount required to form the silicide. The reaction is $SiO_2 + 3C = 2CO + SiC$.

Silicon Carbide Products. The chunks removed from the furnace are in part stored in the yard, in heaps which again form a striking sight, especially on a sunny day. When needed, the chunks are crushed in steel edge-runners, the pans of which revolve while the corrugated steel wheels are stationary. The crushed crystals are washed in water, boiled in sulfuric acid and later in caustic soda, dried, then sieved, the finer crystals on long narrow screens which move forward with a slow motion, backward with a jerk. Coarse crystals are made into large wheels (10 to 36 inches in diameter), smaller crystals are for small wheels.[10] There is an infinite

[9] "Temperature measurements in commercial silicon carbide furnaces," by Raymond R. Ridgway, *Trans. Electrochem. Soc.*, **61**, 217 (1932).

[10] The sizes of particles are also varied in any given-sized wheel according to the degree of smoothness desired.

variety of sizes and shapes. Crystals which pass a 50-mesh screen form a rather coarse grinding powder; those that pass a 150-mesh screen form a fine one. A large percentage of dust is unavoidably produced, which has no value as an abrasive; it is used in the refining of steels. Grinding wheels and tips for dental instruments form a considerable outlet. Grinding compounds for automobile valves, for instance, are silicon carbide powder, in two sizes, set in a calcium soap jelly. Cloth and paper coated with crystals are extremely efficient and replace to a great extent the older emery cloth and sand paper. Honing stones and sharpening tools for farm implements find a ready market.

In order to make grinding wheels, the crystals are mixed with a thin clay containing powdered feldspar and flint, to form the approximate shape; after drying, the correct shape and size are made by trimming with power-driven knives. The wheel is then ready for firing; this is done in coal-fired kilns, similar to those used in potteries.[11] The temperature is controlled by means of pyrometric or Seger cones and by the color and length of the flame. The baking requires 10 days; the complete cycle is 14 days for a kiln. After firing, the wheel is inspected, tested by spinning it at a rate in excess to the stated working rate, and if passed, is then ready for shipment.

Instead of clay, a binder of rubber, or of synthetic resin, is used, with excellent success.

Silicon carbide wheels, stones, and cloths are black or gray. Products which have similar uses are made from fused aluminum oxide, obtained by firing bauxite; these products are yellow.

Electro-orientation.[11a] In the manufacture of so-called sand paper, which may have sand or alundum or some other artificial abrasive, the deposition of the abrasive grains onto the paper or cloth backing is done under the influence of electrostatic charges, with the result that all the grains adhere to their backings with their sharpest point uppermost. Further, the grains are more evenly spaced. The joint result of these improvements is to give the abrasive paper about 35 per cent increased cutting quality. In the course of application the particles are charged with high voltage electricity, and move from one electrode to the other, rotating, so that their lines of longer dimensions are parallel to the direction of force; hence, the manner of seating. Particles so charged repell each other equally, and this leads to equal spacing. The potential applied is 100,000 volts.[12]

It might be remarked in passing that coarse sand paper has 12,000 grains per square inch, while fine sand paper has up to 35 million.

Fused Aluminum Oxide. Another artificial abrasive which is made with the help of the electric furnace is artificial emery, a crystalline alumina (Al_2O_3), known in the trade under the names of "alundum" and

[11] Chapter 10.

[11a] A branch of Applied Electrokinetics.

[12] "Electrocoating sand paper—a method for procuring increased abrasiveness," *The Electrical Review*, London, **118**, 121 (1936).

"aloxite." [12a] The naturally occurring crystalline alumina is corundum, which may be transparent and blue (sapphire) or red (ruby); when less pure and colored brown or black, it is emery. Its hardness is 9 on the scale on which diamond is 10 and graphite 1. Its value as an abrasive is high; the yearly tonnage is about five times the tonnage of the silicon carbide (for the United States and Canada). Artificial emery contains about 95 per cent alumina; its color varies from white to yellow and brown.

Alundum is made from bauxite, a hydrated alumina which contains iron oxide in amounts varying from 1 to 20 per cent; it also contains some silica and other impurities (titanium). The bauxite is first calcined, then mixed with fine coke and iron borings in amounts depending on the silica present, and subjected to the heat of a combined arc and resistance furnace. The charge of 21,000 pounds may consist for example of 73 per cent bauxite, 5 per cent fines, 3 per cent coke, and 2 per cent iron; the bauxite is (here) 78 per cent pure. This furnace, one of a bank of eight, is circular 6 feet in diameter and consists of a water-cooled steel shell lined with a wall of alumina (removable) and fitted with a carbon hearth; two suspended electrodes with single-phase current furnish the heat. The furnace is 7 or 8 feet in diameter and 5 feet deep; the operation is intermittent. As the smelting progresses the furnace receives more of the charge until finally it is full. The electrodes are hung by a cable which is wound on a drum, and constantly move up and down, a correcting action which maintains the current through the furnace constant. If the electrodes dip low, more current enters; the greater current actuates a motor, raising its speed, which is translated mechanically into an up and down motion. Too little dip means less current and a lower speed. As the electrodes wear, the cable automatically lowers them. To some extent a separation takes place; the metallic impurities (ferro-silicon) settle to the bottom, the fused alumina floats on top. The furnace is cooled, the removable wall lifted out, which permits a crane to lift out the ingot, weighing about 10 tons. The cycle of the furnace is 24 hours; the current 130 volts and 500 kilowatts; the electrodes are carbon. The mass is broken, sorted, crushed, washed, and purified by chemical treatment; it is made into wheels, sharpening stones, and grinding powders by methods similar to those which have been described for silicon carbide. A considerable portion of the product serves to make refractories, in brick and other shapes.

A pure white and chemically pure alumina crystallized in the electric furnace is also made, in fact to the extent of 10 per cent of the total crystallized alumina production. It is made from pure alumina (purified by the Bayer process, see chapter 18) with no addition of carbon, and with graphite electrodes in the furnace. Wheels made from this white alumina grind cooler.

Boron carbide. Boron carbide, a comparative newcomer, is made

[12a] Also diamantin, electrit, lionite, exolon.

by heating boron oxide with carbon in an electric furnace [12b] to a temperature of 2400° C. (4352° F.); the product is harder than tungsten

$$2B_2O_3 + 7C = B_4C + 6CO$$
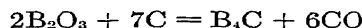
carbide, silicon-carbide, and crystallized alumina. It is black, and has a glass-like fracture. In powder or grain form, it serves as an abrasive for special purposes; its main use at the present time is in its molded form. When heated to a high temperature under a high pressure, the powder forms a block, with the shape of the mold; the boron carbide liquefies enough to be self-bonding. The nozzles for sand blasting equipment are made of this molded boron carbide to advantage.[12c]

TABLE 30.—*Artificial Abrasive Products, 1935, United States.*

Artificial abrasives
Grinding wheels	$21,335,222
Abrasive grains	4,738,419
Abrasive paper	11,192,055
Abrasive cloth	6,565,229
Total artificial abrasive products	$50,122,230

CALCIUM CARBIDE

To the development of the electric furnace is due another substance which was not known before, namely, calcium carbide. It is formed when lime and coke mixed are heated to a temperature of 2000° C. (3632° F.) or higher. Calcium carbide, CaC_2, is important chiefly because with water it forms acetylene, used for lighting and for the steel-cutting and welding torch, but in addition it forms the starting point for one of the several methods of fixing atmospheric nitrogen (cyanamid).[13] It was in this latter respect that it became of paramount interest to the public during the recent war emergency; a plant was constructed at Muscle Shoals, Alabama, which contained very large furnaces.[13a] The carbide furnaces fall in the class of combined resistance and direct-arc heating, that is, the heat is due in minor part to the resistance of the raw materials and product to the passage of the current, in major part to sparking across the charge.

A modern carbide furnace is shown in Figure 110; the long dimension may be 30 feet or more. The charge is 60 per cent lime, CaO, and 40 per cent coke. The current is applied through three suspended graphite electrodes, which are adjustable; an idle electrode is formed by the layer of carbon over the bottom. The reaction is $CaO + 3C = CaC_2 + CO$;

[12b] U. S. Patent 1,897,214, to Raymond R. Ridgway.
[12c] Trade names for boron carbide are Norbide, Borolon, and others.
[13] Chapter 6.
[13a] The intention was to make calcium carbide, then calcium cyanamide, then by the action of steam in autoclaves on the cyanamide, ammonia. This latter was then to be oxidized catalytically, and nitric acid made. The acid after concentration to 100 per cent was to be used for the nitration of cellulose for munitions. In peace time, the acid would serve to make sodium and calcium nitrates, which are fertilizer materials. The war ended before the plant could be put in operation. Since then, the method of making ammonia from calcium cyanamide has become obsolete. Muscle Shoals as a power plant is a distinct and separate consideration.

the carbon monoxide evolved was wasted at one time, but is now frequently saved for synthetic reactions. The calcium carbide is produced in the form of a melt, and is tapped continuously. No refractory except carbon will withstand molten carbide. It is customary, therefore, to build the furnaces very large, and to depend upon a thick layer of semifused material as the actual working lining of the furnace. In consequence, the active part of the furnace is only a small zone immediately surrounding the electrodes; the active charge is only a very few tons.

The raw materials, limestone and coke or coal, must be carefully selected, particularly if the carbide is to be used for acetylene production. The limestone should contain no phosphates or almost none, for these form phosphides later which on burning leave a white deposit; it must be free from magnesium carbonate, for magnesium does not form
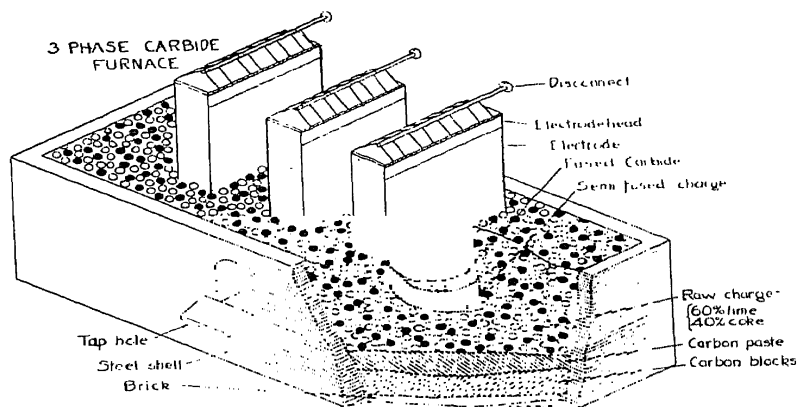
Figure 110. — A carbide furnace, with three electrically connected electrodes, and an idle or bottom electrode. The product is tapped and the operation is continuous. (Basic sketch due to the courtesy of the American Cyanamid Co., New York.)

a carbide and the presence of its oxide in the charge causes a waste of current. The coke is hard coke, washed free of dust, selected further for low ash (3 per cent is very low); anthracite is used in England to some extent. Were no selection made, it might well happen that the carbide would be so viscous, because of impurities, that it would not flow.

The liquid carbide flows into "chill cars" of 1000 pounds capacity; the carbide contracts on cooling, so that it is readily dumped. If it is intended for acetylene production, it passes through a jaw crusher [14]; then through very slow rolls [14] to give a minimum of dust; the pieces are screened to size, 2-inch pieces for large generating tanks, pea sized for miners' lamps. For making cyanide, the crushed carbide is sent through a continuous pebble mill, which gives a powder, 80 per cent of which passes a 40-mesh screen; this then is fed to a tube mill [14] (pebbles), which gives "milled carbide," 85 per cent of which passes a 200-mesh screen. To remove the possibility of forming an explosive mixture from acetylene, generated by accidental moisture, with air, the grinding is done in an atmosphere of nitrogen.

[14] Chapter 44.

The crude carbide is 83 per cent CaC_2, 14 per cent lime (CaO), and 1 per cent carbon; it contains small amounts of silicides, phosphides, and sulfides. It will be evident that the raw materials must be carefully selected, when it is remembered that there is no slag which can be rejected; whatever impurities enter the furnace, and are not volatilized, will appear in the carbide.

The electrodes wear away during operation, and the merits of the several furnaces must include a reasonably low carbon consumption; in the furnace described above, it is 70 pounds per ton of carbide.

An important figure is the number of pounds of carbide produced per kilowatt-hour consumed; from the figures given for this furnace it is 2 kilowatt-hours for 1 pound of crude carbide; or 4.3 kilowatt-hours for 1 kilo of crude carbide; expressed still differently, it is 9.2 pounds of product per horsepower day. The current efficiency is then about 62 per cent.

Other Products of the Electrothermal Furnace

The ferro-alloys are described in the chapter on steel.

Carbon disulfide is a product of an electrothermal furnace of shaftlike construction [15]; the materials are charcoal and sulfur; the charcoal is fed from the top, and is swept by the outgoing vapors of the product; the sulfur is fed through channels in the walls to the base of the furnace. The electrodes are placed just above the hearth, and the heat is due to the resistance of the charcoal to the passage of the current; this is therefore a resistance furnace with direct heating. The vapors are condensed by cold water and the liquid redistilled. Furnaces in which fuel heat is applied are also in successful use. Carbon disulfide is flammable and, mixed with air in certain proportions, explosive; the furnace operates very smoothly, however. The product is of value as a solvent; it is used to make carbon tetrachloride, and in the vulcanization of rubber [16]; but its most important use is in the manufacture of viscose silk or rayon.[17]

An electrothermal furnace has been described recently (1932) which receives sulfur vaporized in a separate lower chamber. The furnace proper or upper chamber has 2 electrodes; the carbon is fed as charcoal with a small amount of broken hard graphite pieces introduced just over the electrodes in order to lower the resistance. The carbon mass is kept at red heat.[18]

Other Patents

U. S. Patent 1,859,856, production of silicon carbide by charging a mixture of calcium silicate slag containing 85 per cent combined CaO and SiO_2 and carbonaceous material into an arc type furnace; 1,872,202, on making calcium carbide, by forming briquets of coke, lime, and water, drying and smelting them with additions

[15] "The manufacture of carbon bisulfide," by E. R. Taylor, the inventor of the process, *Ind. Eng. Chem.*, **4**, 557-9 (1912).
[16] Chapter 39.
[17] Chapter 22.
[18] U. S. Patent 1,849,140.

of lime and coke; 1,705,697, 1,705,717, resistance type furnace; 1,737,566, electric furnace for the production of carbon bisulfide; 1,979,052, electric resistance furnace; 2,005,956, method of making abrasive metal carbides, and apparatus; 1,893,106, method and apparatus for electrically fusing nonconducting materials.

PROBLEMS

1. The charge for a furnace run for making silicon carbide is 32 tons of mixed materials, coke, sand, and sawdust, in the proportions specified in the text. 16,000 pounds of crystals of silicon carbide are obtained. Let the sand be 98 per cent SiO_2. What percentage of the total possible product is the amount actually collected?

2. A calcium carbide furnace produces 48 tons of crude carbide, 85 per cent CaC_2, per day. The current is 130 volts, 60,000 watts. Find the kilowatt hours for each pound of crude carbide, and for a pound of 100 per cent material. What is the horsepower-day per pound? Use the appendix for conversion figures.

3. What is the yield of carbide in Problem 2 on the basis of the lime used, if the lime is 97 per cent CaO?

4. The heat effect in the formation of calcium carbide is included in the reaction below:

$$CaO + 3C = CaC_2 + CO + 108.0 \text{ Calories.}$$
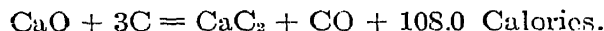
Changing these to kilowatt hours gives a theoretical energy consumption of 1.96 kwhr. per kilo of CaC_2. This is on the basis of 100 per cent current efficiency, and for 100 per cent carbide. It also refers to room temperature, while in practice, the reaction takes place at near 2000° C., necessitating a higher consumption of current for heat production, and making up for heat losses by radiation. At 50 per cent energy efficiency, the figure becomes 3.92 kwhr. per kilo of product. The consumption given in the text is somewhat higher. Check all these figures; 1 kwhr. = 860.5 Calories, which figure should also be checked by the student.

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"Formation and dissociation of silicon carbide," Otto Ruff, *Trans. Electrochem. Soc.*, 68, 87 (1935).

"The preparation and properties of so-called 'beta-alumina'," Raymond R. Ridgway, A. Albert Klein, Wm. J. O'Leary, *Trans. Electrochem. Soc.*, 70, 71 (1936).

Chemical decompositions may be brought about by the electric current at high temperatures, in a bath of fused salts, as well as at low temperature, in water solution; in such cases, the electrolytic cell may well be called an electrolytic furnace. Another modified application of the cell permits chemical changes consisting of oxidation, rather than decomposition as is the case of the manufacture of caustic soda. Both these applications have, in the hands of the chemical engineer, yielded new commercial products, or cheapened some already known.

Chapter 18

Products of the Electrolytic Furnace, Aluminum, Magnesium, Sodium; and Products of the Electrolytic Cell Other than Caustic

The decomposition of salt in water solution, resulting in the formation of caustic soda and chlorine, by passing direct current through the cell, is the most familiar instance of electrolytic decompositions.[1] Fused salts, free from water, at temperatures which may be red heat and higher, are similarly decomposed. The attempt to treat fused sodium chloride in that way resulted in failure until the advent of the Downs cell, a recent development. The electrolytic decomposition of aluminum oxide dissolved in fused cryolite ($AlF_3.3NaF$) has been completely successful and constitutes the present method for the manufacture of aluminum metal; a similar process serves for magnesium. The electrolysis of fused salt is the modern method of manufacturing sodium metal; its comparatively low price permits its use for the preparation of a number of materials which could not otherwise be made, including sodium peroxide and sodamide.

The three processes just given are straightforward decomposition reactions, by the direct electrical current; another type of reaction is performed in the electrolytic cell, chiefly with hydrous electrolytes, namely, that of oxidation, at the anode. Examples are the change of sulfuric to persulfuric acid, of manganates to permanganates; these are presented later in this chapter.[2]

ALUMINUM

The electrolytic process for the manufacture of aluminum was invented by an American, Charles M. Hall[3]; at about the same time, the French inventor Héroult devised essentially the same process. Previously, aluminum had been made by the action of sodium metal on

[1] Chapter 5.
[2] Oxidation may also be considered as a partial loss of electrons on the part of a negatively charged ion, at the anode (the plus pole).
[3] U. S. Patent 400,665 (1889); the Hall process was made possible by the use of the Cowles internally heated furnace. References to the famous litigation which grew out of this circumstance will be found in "The law of chemical patents," Edward Thomas, New York, D. Van Nostrand Co., 1927.

cryolite and other double salts of aluminum; the cost was high, because sodium at that time was made by reducing sodium oxide by means of coal in retorts. The production was small.

The electrolytic furnace in the Hall process operates at a temperature of 950° C. (1742° F.) It partakes of the character of an electric furnace and of an electrolytic cell; a part of the current is transformed into heat by the resistance of the materials in the charge, hence the furnace must be classed among the resistance furnaces with direct heating.[4] By means of this heat, a melt is formed which suffers decomposition by the passage of more current. No outside heat is necessary, as was thought in the early days of the process.

The raw material electrolyzed in the furnace is aluminum oxide, Al_2O_3, dissolved in cryolite, $AlF_3.3NaF$; the latter is obtained from Greenland where extensive deposits occur; in Germany, the demand is great enough to permit the manufacture of an artificial cryolite. The alumina must be very pure; it is made from bauxite[5] by various processes, of which the Bayer is the best known. This process consists of roasting the bauxite in order to destroy organic matter and to oxidize the iron; this is followed by digestion with caustic soda solution; the alumina dissolves. The liquor from the digester is diluted in order to precipitate all the iron, and filtered; the clear filtrate, containing sodium aluminate, is agitated with precipitated alumina from a previous batch, when about 70 per cent of the dissolved alumina precipitates.[6] This is in turn filtered; the solid is dried and calcined, and is then the pure alumina ready for the electrolytic furnace; the filtrate is concentrated, decanted from the sodium silicate which separates out in the strong caustic, and used over again.

The furnace consists of a steel box 8 feet long, 4 feet wide, and 4 feet high, sometimes mounted on rockers so that the whole furnace may be tilted. The box is lined with fire-bricks, and these are covered with a carbon lining; in the bottom, several carbon blocks are buried in the lining; both lining and the carbon blocks conduct the current. The bottom is slightly inclined so that the molten metal can be run to a tap hole. The fused cryolite is contained in the space between the lining of the sides and bottom; the anodes are suspended from above and may be lowered as they wear; they are made of hard carbon generally. During operation, the bottom is covered by melted aluminum, which forms the cathode; the anodes are lowered to within 2 inches of the metal. The number of anodes per furnace varies between 4 and 12, arranged in single or double row; they vary in cross-section between 6 and 12 inches square. The number of furnaces varies with the size of the plant; they are usually arranged in banks of twenty-four.

Alumina is added to the fused cryolite at certain intervals; the maximum content of dissolved alumina is 20 per cent, and it is not

[4] Chapter 17.
[5] Chapter 2.
[6] *Chem. Met. Eng.*, **19**, 807 (1918).

allowed to drop below 10 per cent. The melted cryolite is covered with a blanket of alumina, so that the surface of the cell presents a white appearance, with no liquid visible. A certain amount of fluorspar, CaF_2, is also added in order to lower the fusion point. The density of the melted cryolite must be kept lower than that of melted aluminum, otherwise the metal does not collect on the bottom.[7] The reaction is primarily

$$Al_2O_3 = 2Al + 3O; \tag{1}$$
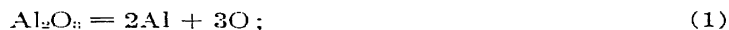
but the oxygen attacks the anode forming carbon monoxide,[8] so that the total reaction is

$$Al_2O_3 + 3C = 2Al + 3CO. \tag{2}$$

The carbon monoxide passes out through the cryolite to hoods placed above the furnaces. The decomposition voltage for alumina at 915° C., dissolved in fused cryolite, and reacting as in (2), is 2.03. The normal drop in voltage per cell is 6 to 7; a rise indicates that more alumina is needed; a slow evolution of gases at the surface indicates the same thing.

Adding alumina to the fused cryolite lowers the latter's density, hence favors the clean settling out of the metal. If it is neglected, some of the metal will be carried upward by the gases, to the anode, there to be oxidized by the atomic oxygen, forming alumina again; the current efficiency[9] would thereby be lowered. This happens to some extent at all times, as well as other disturbances, so that a current efficiency of 70 per cent is considered good. The amperage is 7000 and more; each furnace is tapped once a day, giving 120 pounds of metal per day, for the 8 by 4 by 4 unit.

Aluminum is prized because of its low density, its resistance to corrosion, its good electrical conductivity, and its pleasing color, resembling silver. These properties have led to numerous uses such as for the construction of airships, chemical vessels, kitchenware, electrical transmission lines, and motor car parts. The avidity with which aluminum combines with oxygen has led to its use in deoxidizing Bessemer steel,[10] and in the thermite process.[10]

The strength of aluminum is greatly increased by the addition of small amounts of other metals, and by heat treatment. Duralumin is such a "strong alloy"; it contains 4 per cent copper, 0.5 per cent magnesium, 6 per cent manganese, and the silicon and iron present in the aluminum from the furnace. The alloy is heated to 500° C., quenched, and aged 4 days; the resulting bars have a tensile strength of 60,000 pounds per square inch, equal to that of medium steel, and double that of the furnace aluminum. Another alloy is alpax, with 13 per cent silicon, the rest aluminum.

Aluminum bronze is an alloy of copper with not more than 11 per

[7] Molten aluminum at 950° C. has density 2.36; solid aluminum, 2.58; fused cryolite (impure) 959° C. has density 2.17; solid cryolite, 2.9.
[8] Carbon dioxide is also formed, so that the consumption of carbon is not quite as high as indicated by the reaction given.
[9] Chapter 5.
[10] Chapter 48.

cent aluminum. Magnalium is aluminum with 10 to 20 per cent magnesium, an alloy lighter than aluminum. Lately it has been found that 0.02 per cent sodium increases the strength of aluminum-silicon alloys, favored for castings; and methods have been developed for making 99.98 per cent aluminum metal from less-pure metal.[11] The usual commercial grades for aluminum metal are No. 1, 99.55 per cent Al, and No. 2, 96 per cent Al.

The method below illustrates how even very slight differences in properties may form the basis for successful large-scale operation. An electrolytic bath of cryolite, fused, is used, to which certain amounts of barium floride are added, to adjust the density. Impure aluminum is too heavy, and forms a bottom layer; pure aluminum is lighter by enough so that it floats on the top of the cryolite bath forming an upper layer which can be removed. The impurities stay in the bath. By this process, 99.947 per cent aluminum is produced. As with many other metals, the resisting properties of this aluminum are superior to those of the less-pure varieties.

The production of aluminum in 1935 was 119,295,000 pounds, valued at 18.5 cents a pound. In 1929 the production was nearly twice as great.

MAGNESIUM

Metallic magnesium is made by the electrolysis of fused magnesium chloride, usually containing potassium or sodium chloride, which lower the fusion point, and are unaffected by the current in presence of the magnesium salt. The magnesium chloride may be obtained from mother liquors from natural or artificial brines; or fused carnallite may be used. The apparatus consists of a cast-iron vessel, unlined, and set over a fireplace with oil burner, so that heat may be applied part of the time or all the time. Anhydrous carnallite $MgCl_2.KCl$ melts at 460° C. (860° F.), and magnesium metal melts at 650° C. (1202° F.). The cell is operated just above the latter temperature, so that globules of magnesium form which rise to the top of the fused chlorides. The pot is the cathode, and is connected metallically to a secondary iron cathode, a cylindrical sleeve surrounding the graphite rod in the center of the melt, the anode. By means of a proper construction of the cathode sleeve, a circulation of the melt [12] can be set up which aids the rise of the globules; they reach an annular gutter facing downward, set in the melt near its upper surface. The metal is withdrawn from there, after it has cooled enough so that it no longer takes fire when exposed to air. The second product of the electrolysis is the chlorine; given an anhydrous feed to the cell, the corrosive action of the chlorine is reduced, and it is successfully handled. The decomposition voltage for fused magnesium chloride at 700° C. is 3.01; the operating voltage 5 to 6.

Magnesium metal is also produced from a bath of fused magnesium

[11] *Ind. Eng. Chem.*, **18**, 924 (1926).
[12] U. S. Patent 1,851,817.

fluoride to which calcined magnesium carbonate is added at a constant rate; the fluoride is not consumed because its decomposition voltage is ten fold that of magnesium oxide. Magnesium is purified by distillation in an atmosphere of hydrogen; it congeals at the upper part of the tall retort in large lustrous silvery crystals. When using materials free from heavy metals, no purification is necessary.

Magnesium has a specific gravity of 1.74 at room temperature, still lower than that of aluminum. Its chief uses are as an alloy [13] in aeroplane construction and for a flushing of radio tubes, which it scavenges, removing even traces of gases which pumps and charcoal could not remove. Among its alloys, magnalium is described under aluminum; another is Dow metal, 95 parts Mg, 2 parts Cu, 3 parts Ni. Both are aeroplane materials. Magnesium is also used as a flashlight powder for photography, for flare bombs in the navy.

In 1935 there were sold or used by the U. S. producers 4,241,218 pounds of new magnesium in ingot form; value per pound in 1934 was 26 cents; in 1929 the production was only 1.3 million pounds, the amount sold or used 908,351 pounds.

SODIUM

Sodium metal was made originally by the electrolysis of fused caustic, with the metal as the sole product. Cells holding 250 pounds of melted caustic with a central iron rod as cathode, surrounded by a nickel perforated cylinder as anode, were operated within the range of 315° to 320° C. (599° to 608° F.). The current efficiency was 45 to 55 per cent, the voltage 4.5 to 5.5 per cell. The total reaction in the cell may be written: $4NaOH = 4Na(cathode) + 2H_2O + O_2$ (anode).

The method for the manufacture of sodium metal to-day is the electrolysis of purified and absolutely dry fused salt NaCl. Sodium made directly from salt is much cheaper than sodium made from caustic, since the latter is itself a manufactured article, while salt is found in nature. Besides, a second product, chlorine, is obtained, and in a high state of purity. The Downs cell [14] operates on fused salt. The operation is continuous; the sodium produced is collected in a separate compartment, and withdrawn from there periodically. The chlorine is sent out free from moisture. Several details of its construction are shown in Figure 111.

At the carbon anode, 1, the chlorine gas is evolved, and is collected in the dome 3; it passes out under its own pressure. The cathode, 2, is an annular iron or copper piece, which surrounds the circular anode. The cathode is hooded by two metal screens. Sodium metal is generated at the cathode and is collected in the sodium collector marked 4, just above the cathode. The melted sodium is lighter than the fused salt, and rises readily. The collector is provided with a riser 5 which delivers the sodium to a closed compartment, from which it is withdrawn at stated

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[13] "Chemische Technologie der Leichtmetalle und ihrer Legierungen," F. Regelsberger, Leipzig. Otto Spamer, 1926.
[14] U. S. Patent 1,501,756 (1924), to J. C. Downs.

intervals. The level of fused salt in the bath is maintained high enough to force the column of sodium along the delivery arm in the riser. Fresh salt is introduced at 7, and as it fuses it loses any water it may contain, which passes out to the room.

Sodium chloride fuses at 800° C. (1472° F.), but the cell is operated at a lower temperature, such as 600° C. (1112° F.), thanks to the addition of materials to the bath which do not suffer decomposition. This lower temperature avoids the sodium metal fog which baffled all efforts at collection of the metal produced. Furthermore, at such lower temperature, the cell has longer life, and the chlorine is handled more easily. A certain amount of hydride of sodium (a white solid) forms, and gives rise to small explosions. The current efficiency is high, above 80 per
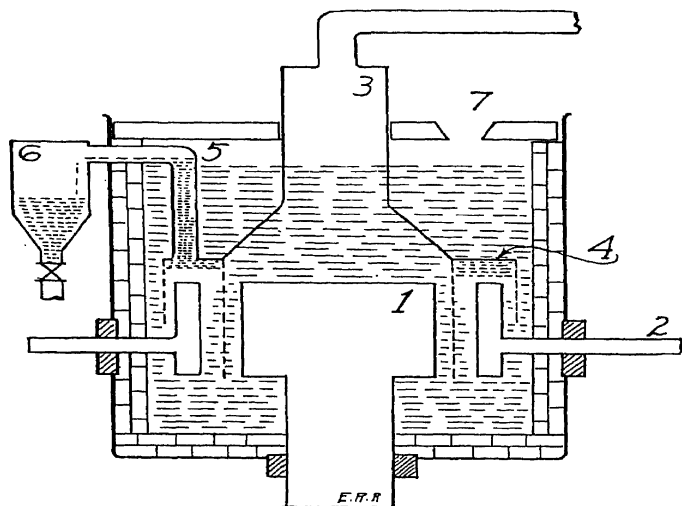
FIGURE 111.— The Downs cell, producing metallic sodium from salt. 1, carbon anode; 2, iron cathode; 3, dome for escaping chlorine; 4, annular sodium collector.

cent, and the cells are as large as "20,000 amperes units." The decomposition voltage for fused NaCl at 600° C. is 3.93; operating voltage, 7 to 8. The Downs cell is an American invention, and its worth was proved in American plants; since 1929, it has been adopted in Germany.

An electrolytic cell-furnace for sodium, which is reported in successful operation in Germany, has a long knife-like iron cathode running longitudinally in the center of the cell, with an internal slit-like passage for the upward trip of the sodium metal, and an inclined cover piece, also part of the cathode, to deliver the molten metal to an outer receptacle.[14a]

Sodium sells at 20 cents or so a pound. It is a soft solid, and is shipped in the form of 12-pound bricks, packed in air-tight drums. Sodium is an industrial chemical; it is the raw material for sodium peroxide, sodium cyanide, and is the basis of the lead alloy used in manufacturing tetraethyl lead; it may be used to improve the structure of

[14a] U. S. Patent 1,820,844; of interest also 1,074,988 and 1,092,178.

various alloys, to purify molten metals, in organic manufacturing condensations and reductions. It may be made into a chlorine-free sodium hydroxide, by adding the metal, with suitable precautions, to a concentrated hydrous caustic solution. The properties listed in Table 31 may lead to other applications.[15]

TABLE 31.—*Physical Properties of Various Fluids Suitable for Transmission of Heat Including Metallic Sodium.*

Property	Sodium	Mercury	Tin	Meprolene Oil	Diphenyl $(C_6H_5)_2$	Water
Melting point, °C.......	97.5	-38.8	232	0±	69	0
Boiling point						
760 mm.	883° C.	357	2270	300±	255	100
75 mm.	677° C.					
13 mm.	565° C.					
Density, gms./cc.	0.834 (98–883° C.)	12.9 (100–400°)	6.93 (232–400°)	0.91 (20°)	.85 (255°) 1.04 (20°)	0.998 (20°)
Density, lbs./gal........	6.9	107	57.5	7.6	8.7	8.3
Specific heat, cal./gm...	.33 (100° C.)	.033 (20°)	.058 (250°)	0.5±	.559 (300°)	1.0
Thermal conductivity	0.21	0.02	0.15	0.004	....	0.0013
Viscosity coefficient......	....	0.01 (200–300°)	0.01± (250°)	1.0±	....	0.010 (20°)
Heat of vaporization, cal./gm.	1100	65	621	....	74.4	539

Sodium Peroxide. Sodium peroxide Na_2O_2, a white powder, is made in two stages. First, the metal is placed in a revolving steel drum with dehydrated air passing over it; there is formed sodium oxide, Na_2O. This white powder is transferred to a second revolving drum set in brick work so that heat may be applied; dry oxygen is passed into the heated drum, until no more is absorbed. The product now is the peroxide, Na_2O_2. It is valuable as an oxidizing agent for a number of minor chemical operations; it serves to make hydrogen peroxide, metallic peroxides, perborates, and other "per" compounds. It has gained in importance of late years because it is used in the manufacture of benzoyl peroxide, called Lucidol,[16] the bleaching agent for white flour. The benzoyl peroxide is made from benzoyl chloride and sodium peroxide; it is a white powder. $2C_6H_5 . CO . Cl + Na_2O_2 = C_6H_5 . CO . O . O . OC . C_6H_5 + 2NaCl$. For use in the flour mills, the benzoyl peroxide is diluted with calcium phosphate, and is then called Novadelox.[17] The application is by running in a small stream of Novadelox into the regular stream of flour from the spout, as delivered to the bins; there is no other mixing. After a day, the bleaching agent has done its work. It is used in such small amounts that no trace of it can be found by chemical means.

Sodamide. Sodamide, $NaNH_2$, a solid, is made by the action of dry ammonia on metallic sodium; it is important in the synthesis of indigo.[18] Heated with carbon to 800° C. (1472° F.), sodamide is changed [19] to *sodium cyanide*, $NaCN$,

$$2NaNH_2 + 2C = 2NaCN + 2H_2,$$
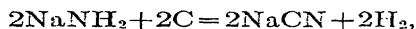
[15] Sodium has been used as a liquid partly filling the hollow stem of the valve in an aëroplane motor, in order to dissipate heat which otherwise would have no escape.
[16] U. S. Patent 1,380,334.
[17] U. S. Patent 1,381,079.
[18] Chapter 28.
[19] German Patent 148,045.

which is run off as a liquid from the furnace and may be cast into convenient shapes (cyanide egg). It is customary to combine the two steps when making cyanide, and to place sodium metal and carbon as charcoal in the covered reaction pots (iron) and pass in the ammonia gas. Heat is applied from the outside; the hydrogen is allowed to burn on reaching the air, or is sent to a gas-holder for re-use in making direct synthetic ammonia.

POTASSIUM PERMANGANATE

The step in the manufacture of permanganate which may be performed in an electrolytic cell is the change of potassium manganate, K_2MnO_4, green in color, to potassium permanganate, $KMnO_4$, which is red; this
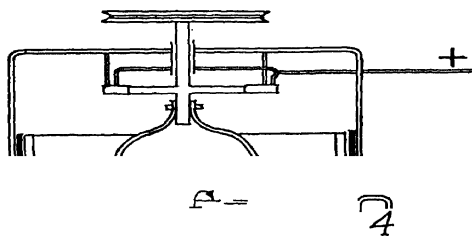
FIGURE 112. — Permanganate oxidation cell. 1, rotating wire-netting anode; 2, inlet pipe for liquor, forming also cathode; 3, sulfur insulation; 4, outlet for liquor.

change is an oxidation and takes place at the anode. The liquor at the same time becomes alkaline, due to the formation of potassium hydroxide. A cell which has been found suitable for this oxidation is shown in Figure 112. The changes may be expressed in three reactions, which are summarized in the fourth:

$$
\begin{array}{c}
\quad\quad\quad\quad H_2O \quad\quad\quad\quad O \quad +2H \\
2K_2MnO_4+ \quad O \quad\quad 2KMnO_4+K_2O \\
\quad\quad K_2O+H_2O \quad\quad 2KOH \\
\hline
2K_2MnO_4+2H_2O \quad\quad 2KMnO_4+2KOH+H_2
\end{array}
$$
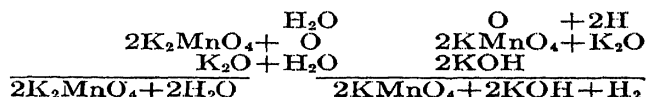
This consideration has led to the term "anodic oxidation." Expressed in terms of ions, the manganate ion $MnO_4^=$ loses one electron at the anode, and becomes MnO_4^-, while at the same time one potassium ion K^+ is discharged at the cathode and becomes potassium metal, which

reacts with water to form potassium hydroxide and hydrogen; two hydrogen atoms pass off as one molecule of hydrogen gas.

$$2K^+ + MnO_4^= + H_2O \qquad K^+ + MnO_4^- + KOH + H$$

The complete process of manufacture comprises a fusion of manganese dioxide, MnO_2, with a caustic potash, KOH, in a muffle furnace with circulation of air, when the potassium manganate forms. The product of the furnace is leached, and the solution, after a treatment to remove most of the excess caustic potash, passed through the cell. The potassium permanganate is so insoluble that some of it separates in the cell; on concentration, another part is obtained.

Another procedure independent of current consists in passing carbon dioxide into the manganate solution, with the production of permanganate and hydrated manganese dioxide (artificial pyrolusite) as a byproduct.

$$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + MnO_2 + 2K_2CO_3$$

Potassium dichromate may also be made with the aid of the electrolytic cell. In general, however, it is made in the standard way. The ore chromite is crushed, powdered, and fused with alkali carbonate; the cooled melt is leached, and the chromate obtained. The dichromate is made by treating the chromate with mineral acid.

Chromic acid in red crystal form is made by treating the chromate or dichromate with sulfuric acid of high concentration, and filtering through filtros or wool felt.

Ammonium Persulfate. Ammonium persulfate, $(NH_4)_2S_2O_8$, a white crystalline solid only slightly soluble in water, is made by the electrolysis of a water solution of ammonium sulfate containing sulfuric acid. The anode is a small platinum plate (hence high current density), the cathode a larger lead plate (hence low current density); the bath is kept cold by cooling coils in which brine circulates (10° C.). The ammonium persulfate appears at the anode where it precipitates. This product is useful as an oxidizer for many minor purposes, and as a solvent for silver in photography.

Hydrogen Peroxide By Electrolysis. Hydrogen peroxide, H_2O_2, is sold in the form of a water solution, in strengths varying from 3 to 30 per cent. It is made by the hydrolysis of persulfuric acid, $H_2S_2O_8$, obtained by anodic oxidation of sulfuric acid at low temperature. Another way is by the intermediate formation of ammonium persulfate, and subsequent treatment with sulfuric acid to form persulfuric acid, which is then hydrolyzed; after the hydrolysis, the hydrogen peroxide formed is distilled under reduced pressure. The ammonium persulfate method has been developed into a continuous process [20]: Ammonium sulfate and sulfuric acid in the proportions to form ammonium bisulfate $(NH_4)HSO_4$ are electrolyzed cold, forming ammonium persulfate at the anode; the salt is removed and distilled rapidly with sulfuric acid, at reduced pressure. Hydrogen peroxide

[20] U. S. Patent 1,234,880.

and water pass over. The residual liquid is cooled and used over again in the cells; ammonium sulfate which separates out as a solid is also used over again. Theoretically at least, only water and current are consumed. The reactions are:

$$2NH_4HSO_4 = (NH_4)_2S_2O_8 + H_2;$$
$$(NH_4)_2S_2O_8 + H_2SO_4 = H_2S_2O_8 + (NH_4)_2SO_4;$$
$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2.$$
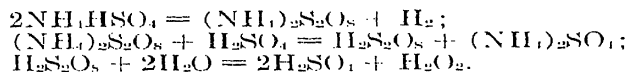
Another method for the preparation of hydrogen peroxide is the *barium peroxide method,* which retains some importance only because it has a salable by-product, blanc fixe. Barium oxide is heated to 600° C. and dry air passed over it; barium peroxide, BaO_2, is formed. Both the oxide, BaO, and the peroxide are white solids. The peroxide of barium is hydrated by a special steam treatment, producing a creamy fluid essentially of formula $BaO_2.8H_2O$. This is mixed with a mixture of one-third phosphoric acid in dilute sulfuric acid in a large tank, liberating hydrogen peroxide and precipitating barium sulfate or blanc fixe.[21] The latter is filter-pressed, washed, and sold wet to paper mills. The solution of hydrogen peroxide is adjusted to proper strength by distillation.

A commercial strength of hydrogen peroxide solution is known as 3 per cent H_2O_2, or "10 volumes," which means that the solution will liberate, under standard specified conditions, oxygen to the extent of 10 times the volume of the solution; the 30 per cent strength liberates 100 volumes of oxygen, and is properly designated "100 volume" peroxide.

A third method for making hydrogen peroxide consists of treating sodium peroxide in solution with sulfuric acid; a stronger grade is obtained by this method, in the first solution. The sodium sulfate formed, unlike the barium sulfate, is soluble, and is removed from solution by adding sodium fluoride and cooling to −2° C., under which conditions the sodium sulfate separates out. The finished product still contains about 3 per cent of mineral matter, which, however, does not generally interfere with its applications.

The uses for hydrogen peroxide are increasing at a rapid rate; it serves as a bleaching agent, e. g., in the felt hat industry; it may be used for the manufacture of metallic peroxides, and like sodium peroxide, for making "per" salts. It is being manufactured at the rate of many tons a day. The 30 per cent H_2O_2 grade, on contract, sells for about 20 cents a pound.

OTHER PATENTS

U. S. Patent 1,839,756, on an apparatus (cell) for electrolyizing fused NaCl, and 1,826,773, on the method of salt feed; on the collection of magnesium in the cell, German Patents 344,427 and 302,024; on the electrolysis of NaOH for sodium, German Patents 344,427 and 302,024; U. S. Patent 1,875,760, electrolysis of molten magnesium chloride; 1,820,022, production of metallic magnesium by electrolysis of fused $MgCl_2$; 1,878,939, metallic aluminum by thermal reduction of oxide ores; 1,833,806, electrolytic refining of aluminum; 1,770,940, chemically pure aluminum by electrolysis; 2,021,384, removal of acid from peroxide solutions, to Joseph Reichert; 2,008,726, storing and handling hydrogen peroxide solution; 2,004,809, 2,022,860,

[21] Chapter 31.

on stabilizing hydrogen peroxide; 2,017,440, on hydrogen peroxide purification; 2,022,650, on hydrogen peroxide process; 2,054,303, on the reaction of sodium with hydrocarbons, to Norman D. Scott; 2,065,744, on the production of sodium perborate.

PROBLEMS

1. An aluminum furnace is to produce 120 pounds of metal per day. How much aluminum oxide will be required, if the yield is perfect, and how much carbon will be consumed?

2. A brine contains 3 per cent $MgCl_2$. In order to produce 1 ton of magnesium how many gallons of brine must be concentrated, and how much chloride must be fed into the cell? The recovery in each case may be assumed 100 per cent.

3. A cell produces 600 pounds of sodium. The feed is continuous, and steady over the day. How much NaCl per hour must be fed in, and how many pounds of chlorine are collected? Let the chlorine recovery be 91 per cent.

4. The decomposition voltage is found by the simplified expression $E = Q$ in gram calories times $4.1834 \div 96580 \times n$. E is then in volts; n is the number of gram equivalents involved. Q is the heat of all the substances involved in the reaction; the heat is positive for the substances on the left, negative for those on the right. The calories obtained by multiplying the mole heat (specific heat $\times$ molecular weight) are deducted from the Q value originally found; the reduced value serves to compute E.

For fused salt at 600° C., the figures are: (97,700 calories − 585 × 12.0 = 90.680); this × 4.183, then, divided by 96,580 gives 3.93v.

5. The heat of formation at 15° C. of $MgCl_2$ is 151.0 Calories. Its mol heat 18.5. Electrolytic decomposition is performed at 700° C. What is the decomposition voltage, remembering that $n = 2$?

6. The heat of formation of Al_2O_3 is 378 Calories. The heat of formation of CO is 26.2 Calories. If electrolysis takes place at 915° C., and the mol heat of alumina is 20.4, what is the decomposition voltage?

7. What are the theoretical weights of the metals deposited per Faraday (96,580 coulombs) for the cases in Problems 4, 5 and 6, and what are the weights of the several salts decomposed by one Faraday? What are the actual weights, taking into account the current efficiency stated in the text?

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"Hydropower for the production of aluminum," James W. Rickey, *Trans Electrochem. Soc.*, **70**, 185 (1936).

"Recent advances in the aluminum industry." Frances C. Frarey, *Trans. Electrochem. Soc.*, **70**, 131 (1936), mainly applications to construction.

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The utilization of gases on the industrial scale is one of the triumphs of present-day chemical engineering; the seamless steel containers in which some of them are transported, under pressure, are familiar sights on trucks and railway cars. Gases serve as chemical agents, refrigerants, anesthetics, disinfectants; they also serve in beverages, for flames, and to stifle flames.

Chapter 19

Industrial Gases

The gases included in this chapter fall into two groups: hydrogen, H_2, helium, He, oxygen, O_2, nitrogen, N_2, and argon, A, the less easily compressible gases; and chlorine, Cl_2, sulfur dioxide, SO_2, ammonia, NH_3, nitrous oxide, N_2O, carbon dioxide, CO_2, carbon monoxide, CO, acetylene, C_2H_2, and ethyl chloride, C_2H_5Cl, the more compressible gases. At ordinary temperatures, the former do not liquefy in spite of considerable pressure; the latter at ordinary temperature form liquids under rather moderate pressures; hence the content by weight of a standard cylinder for the gases in the first group will be small, for those in the second group, considerable. It follows that gases in the first group will be used as free gases at once upon generation, or will be shipped short distances, from many plants, each serving small territories; while gases in the latter group may economically be shipped long distances, from a few central plants.

In addition to a variety of technical uses, several members of the second group serve as ordinary refrigerants—ammonia, carbon dioxide, sulfur dioxide, and ethyl chloride: to these must be added the newer refrigerants, dichloro-difluoromethane, propane, and butane, which are discussed in Chapter 12. Members of the first group are used as extraordinary refrigerants; for example nitrogen in liquefaction of carbon monoxide impurities in hydrogen.

HYDROGEN

Of late years, hydrogen has become of industrial importance in the direct synthesis of ammonia, in the hydrogenation of fatty oils, petroleum oil fractions, of coal, of hydrocarbons, and single organic substances; its other uses are for balloons and dirigibles, for the hydrogen-air, hydrogen-oxygen, and atomic hydrogen flame.

It is obtained from water gas, producer gas, coke-oven gas, by the removal of the non-hydrogen constituents; it is made by the action of steam on oil refinery gases and natural gas, by the thermal decomposition of natural gas, by steam on heated iron, by the electrolysis of water, and by miscellaneous processes. It is a by-product in the electrolytic cell for caustic, in several fermentation processes, and in others. The choice of a process will be decided by the resources at hand, and by the degree of purity required. Rapid generation with a minimum of appara-

tus in an isolated place may be demanded; in such a case the ferro-silicon process would serve.

The Water Gas and Steam Process, a Continuous Catalytic Process. Water gas [1] with steam in excess is passed over an iron oxide catalyst, just as is done in the Bosch process described in Chapter 6, except that since no producer gas is added, the amount of nitrogen is small. The converter has several trays, on which the catalyst rests. The reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

is exothermic; as the temperature must be maintained at 450° C. (842° F.), the converters are insulated and the incoming gases heated in exchangers. Once the reaction has begun, no outside fuel is required. Three volumes of steam to one of gas are used; the great excess of steam drives the reaction to the right. After passing the exchangers the reacted gas is freed from its steam by water cooling. The carbon dioxide formed, as well as the small amount which entered with the water gas (4 per cent), is removed by scrubbing with cold water while under pressures of 25 to 30 atmospheres, in tall steel towers; under such pressures carbon dioxide is freely soluble in water. The gas leaving the last scrubber has the composition

	Per cent
Hydrogen	92–94
Nitrogen	1–4
Methane	0.5
Carbon monoxide	2–4
Carbon dioxide	small amount
Moisture	small amount

The crude hydrogen may be purified further from carbon monoxide by scrubbing in ammoniacal cuprous chloride solution. The nitrogen impurity may be lowered by careful operation of the water-gas plant. The methane is not wanted, and may be almost avoided by using well-burned coke.

A similar process in which the catalytic agent is lime at the temperature of 450° C. (842° F.) instead of iron oxide has been proposed; its great advantage is that the carbon dioxide is simultaneously removed. Unfortunately this absorption is accompanied by a powdering of the lime granules, as the carbonate forms, and the powder tends to clog the lime towers.

Water Gas Process with Liquefaction of the Carbon Monoxide. There are two processes in which the carbon monoxide is liquefied by cold and pressure and removed in that state, leaving the hydrogen gas comparatively pure. The Linde-Frank-Caro process uses liquid air boiling under a few millimeters of pressure for the final cooling of the water gas already pre-cooled by three steps, first by an ammonia refrigerating system (−35° C. or −31° F.), then in an exchanger wherein the uncondensed hydrogen takes up heat, third by the liquid carbon

[1] Chapter 15.

monoxide separated in the final cooling. The carbon monoxide at the same time boils, and is used as a gaseous fuel. The other process is Claude's, who uses no liquid air, but obtains the necessary final cooling by the expansion of hydrogen from a pressure of 20 atmospheres to a lower pressure while doing work against a piston. The hydrogen is pre-cooled in exchangers by outgoing gases, and by the evaporation of the carbon monoxide which has been previously liquefied.

The hydrogen in coke-oven gas,[2] and in the gas from the petroleum-cracking stills may be recovered by liquefaction of the non-hydrogen components.

Steam on Heated Iron. Many units based on the reduction of steam by iron at an elevated temperature are in use in connection, chiefly, with the hydrogenation of fatty oils. The hydrogen obtained by this process is purer than by the continuous catalytic process; the latter can be purified, but the steam and iron process has the further advantage that it is suited to medium-sized installations, such as are usually required for the hydrogenation of oils. The reaction is

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$
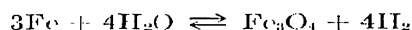
and the oxide formed, when running from left to right, must be reduced at frequent intervals; this is best done by water gas, preferably purified. The iron should have a porous structure and little tendency to disintegrate; a calcined carbonate (spathic ore) has been found suitable. The iron is placed in upright steel retorts, 9 inches in diameter and 12 feet high, grouped in three sets of 12 retorts each. The steaming period (hydrogen production) lasts 10 minutes, the steam traveling upward; the water-gas period lasts 20 minutes, because the reduction of the oxide is slower than its oxidation; the water gas travels downward. A brief purging with steam sends the first hydrogen to the water-gas holder.

By means of such an arrangement a continuous flow of hydrogen is obtained; with the retorts given above, a volume of 3500 cubic feet, about 100 cubic meters, is obtained per hour. The spent water gas is cooled in a scrubber, and burned (for it still contains combustible gases) around the retorts in order to maintain the reaction temperature, 650° C. (1202° F.). The steam reaction is exothermic; the water-gas reaction is endothermic (cooling).

The hydrogen passes out with the great excess of steam employed, in order to drive the reaction to the right. It is cooled in scrubbing towers, and freed from carbon dioxide and hydrogen sulfide by lime purifiers. The gas obtained is 98.5 to 99 per cent pure; by careful purging, using closed condensers instead of scrubbing towers, and other modifications, the purity can be raised to 99.94 per cent. The iron mass lasts six months; the retorts one year. There are many modifications of this process.

The hydrogenation of an oil is retarded appreciably by a carbon mon-

[2] Chapter 6; and *Ind. Eng. Chem.*, **14**, 1118 (1922).

oxide content of even 0.25 per cent; the custom is to produce the hydrogen of as great a purity as careful operation permits, and beyond removing hydrogen sulfide and carbon dioxide, to make no purification.

In the continuous catalytic process 1.25 volumes of water gas are required for 1 volume of hydrogen (on the basis of 100 per cent hydrogen). In the water-gas method which involves removal of carbon monoxide by liquefying it, 2.5 volumes of water gas are required for 1 volume of hydrogen, mainly as fuel for machinery. In the reduction of water by hot iron, water gas is used to revivify the iron, and the amount is 2.5 volumes for one volume of hydrogen produced. The continuous catalytic process has therefore a marked advantage over the other two processes.

Electrolysis of Water. In the commercial cells, direct current is passed between iron electrodes, which may be nickel plated, in a 10 to 25 per cent caustic soda solution. The caustic soda is not consumed; only water needs to be added as the electrolysis proceeds. The hydrogen is generated at one electrode (cathode), the oxygen at the other (anode). Cells differ in the method of gathering the two gases, in other details of construction, and in size. The efficiency varies also, but not very much; an average figure would be 7.5 cubic feet of hydrogen per kilowatt hour, and 3.8 cubic feet of oxygen at the same time. Assuming that the oxygen is wasted, and that the cells are run for the production of hydrogen only, the cost of current will determine the cost of the gas. If the horsepower year is $20, a low figure, 1000 cubic feet of hydrogen will require 40 cents for power. With higher costs for horsepower, the cost for power per 1000 cubic feet will be correspondingly greater. The continuous catalytic process produces 1000 cubic feet of hydrogen for about 45 cents, granted favorable conditions for coke and coal. If both hydrogen and oxygen are required, the electrolytic cells are the proper devices.

The decomposition voltage for the reaction $H_2O = H_2 + \frac{1}{2}O_2$ is 1.48; the operating voltage about 2. The amperage varies with the size and intensity of operation; with maximum load, it may be as much as 1000 amperes for electrodes 40 inches wide by 60 inches high. The electrodes are separated by an asbestos diaphragm, and suspended in cast-iron containers.

One of the large-scale installations[3] for the electrolytic production of hydrogen consists of 306 cells, each with 20 plates. The electrolyte is 25 per cent very pure potassium hydroxide, maintained at 60° C. (140° F.) by the Knowles patented regulator. Each electrode receives 500 amperes, hence 10,000 amperes per cell. The production is 49,000 cubic feet of hydrogen per hour, 99.5 per cent pure, and half that quantity of oxygen. The cells are fed with distilled water. This gas is used in making synthetic ammonia, as part of large auxiliary plants for the manufacture of chemical fertilizer.

Cells operating under pressure and delivering gas at 200 atmospheres

[3]Knowles hydrogen plant at Warfield Works, Consolidated Mining and Smelting Company, of Canada, *J. Soc. Chem. Ind.*, 51, 355 (1932). An interesting cell for the electrolysis of water is the Stuart cell, offered at least in Canada, and which might become available in the United States. (Stuart International Corporation, Ltd., Toronto).

have been proposed; the energy required for electrolysis decreases as the pressure is increased.[4]

Other Processes and By-product Hydrogen. Hydrogen gas is prepared by the thermal decomposition[5] of natural gas, particularly in California, where the state law prohibits the wasting of natural gas. The operation is a cracking of the gas, and is performed in apparatus similar to those used for making water gas. A five-minute cycle is used; the gas is burned to heat up the checkerwork in the generator (2 min.), then the gas, without air, is passed in. Elemental hydrogen gas with suspended carbon particles forms; the carbon is filtered out in bag filters. After 2 minutes, the generator is too cool, and the cycle is repeated.

In the oil industry, hydrogen may be prepared from hydrocarbons in the refinery gases, or in available natural gas, by treating with steam, in the presence of a catalyst or not. The reaction is $CH_4 + 2H_2O = 4H_2 + CO_2$.[6]

The by-product hydrogen from the electrolytic caustic cell is discussed in Chapter 5; from fermentation[7] in Chapter 20, and its utilization in Chapter 25.

In the ferrosilicon process, powdered ferrosilicon containing as much silicon as possible (90 per cent is frequent) is added to a 20 per cent solution of caustic soda at a temperature of 80° to 90° C.; very pure hydrogen is produced. Aluminum in the form of shavings also gives hydrogen with a solution of caustic soda. An alloy of sodium and lead reacts with water to give hydrogen, again of high purity (hydrone). These three processes serve for military purposes and as supplementary plants for emergency or rapid operations.

Helium. This comparatively rare gas is produced in large quantities at Amarillo, Texas; it occurs in a number of natural gases in amounts varying from 0.5 to 7 per cent averaging near 3 per cent. The gas is compressed and cooled, and the non-helium portion removed by liquefaction; 97 per cent He with some nitrogen is obtained.[8]

Helium is used for dirigibles; its value lies in that it forms no explosive mixture with air. The Macon was a helium ship; it was wrecked off the California coast because of a structural defect. Just a while before that the Akron, also a helium ship, was destroyed in a storm over the Atlantic, not far from Barnegat Bay in New Jersey. There is left to the United States only the Los Angeles. The recent catastrophy to the hydrogen-filled Hindenburg (May, 1937) will lead to the use of helium for the German ships. The lifting power of helium is **92 per cent** of that of hydrogen.

[4] *Trans. Inst. Chem. Eng. (Brit.)*, **9**, 154 (1931).
[5] *Chem. Met. Eng.*, **39**, 381 (1932).
[6] *Ind. Eng. Chem.*, **22**, 1030 (1930).
[7] *Ind. Eng. Chem.*, **18**, 1045 (1926).
[8] "The production and uses of helium gas," by R. R. Bottoms, *Aeronautical Eng.*, **1929**, 107; also *Ind. Eng. Chem.*, **11**, 152, (1919).

A portable helium repurification plant has been designed.[9]

It is estimated that the helium reserves already in sight are 10 billion cubic feet, in the United States alone. There is a potential production of 200,000 cubic feet per day from the gas in the boric acid fumaroles in Italy. Canada has some low percentage helium material.

OXYGEN [10]

The great importance of industrial oxygen is due to the usefulness of the acetylene torch for steel welding and steel cutting; and to a lesser extent to the oxyhydrogen flame. The possibility of an extension of its use lies in the increased temperature given by gas when burned in oxygen instead of air, in the blast furnace for iron wherein the amount of useless, heat-consuming nitrogen may be reduced with a saving of coke and an increase in output. Liquid oxygen mixed with powdered charcoal may yet become an important and cheap explosive.[10a]

The industrial method of preparation is the fractionation or rectification of liquefied air. Atmospheric air contains

	Per cent by volume	Per cent by weight
Nitrogen	78.1	75.5
Oxygen	20.9	23.1
Argon	.94	1.29
Carbon dioxide	.03	.049
Water vapor	variable amounts	

The composition of liquid air varies slightly according to the condition of liquefaction; on warming it, there passes out a gas containing 93 per cent nitrogen and 7 per cent oxygen, and there is left a liquid richer in oxygen than the original. Nitrogen boils at $-195.8°$ C., air at $-191°$, oxygen at $-183.0°$, all under the pressure of 1 atmosphere. The difference in the boiling points of nitrogen and oxygen is not quite 13° C., the nitrogen being the most volatile. It is upon this fact that the fractionation is based.

In the liquefaction of air the following steps are included: *a*, the removal of carbon dioxide and dust; *b*, compression to high pressure; *c*, removal of moisture; *d*, cooling to low temperature in exchanger coils; *e*, liquefaction by expansion in the separator.

During the operation of the liquefying system three periods must be distinguished: the starting period, in which the apparatus is brought from room temperature to the low temperature essential for liquefaction (1 hour); the running period, during which the liquefaction proceeds continuously (1 week to 1 month); and the thawing-out period, during

[9] *Ind. Eng. Chem.*, **22**, 1191 (1930).

[10] Based in large part on "Der Sauerstoff," by M. Laschin, published 1924 by Carl Marhold Verlagsbuchhandlung, Halle a.S. Germany (100 pages); and on "Fluessige Luft," by Ludwig Kolbe, published 1920 by Johann A. Barth, Leipzig; the latter book contains several diagrams of complete plants.

[10a] It is the regular explosive now for the iron mines in the East of France (Hayange).

which the carbon dioxide and water, which in spite of all purification accumulate in the system, are thawed and blown out by a stream of warm air. The length of the running period depends upon the efficiency of the purifying apparatus and on the demand, for appreciable stores with which to meet unexpected demand cannot be accumulated in periods of low business activity. The liquefied air is fractionated in single or double columns, and the oxygen compressed in the shipping cylinders.

The cooling during the running period is mainly due to the latent heat of evaporation of the liquefied air. In the starting period, the cooling is due to the expansion of the compressed air against atmospheric pressure, in part to the Joule-Thomson effect.[11] To insure a considerable cooling during both cooling and running period, the Claude system expands a part of the compressed gas after it has been precooled considerably, against the piston of an engine driving a dynamo. In the performance of the considerable amount of work by the gas as such a cooling of 75° C. is secured. Several American plants operate under the Claude license. The description which follows will not include this feature, in order to avoid confusion.

The Liquefaction of the Air. The atmospheric air is drawn into a four-stage compressor, with four separate cylinders, for plants producing 15 cubic meters [12] (530 cubic feet) of free oxygen [13] per hour; for larger plants, five-stage compressors are preferred; three-stage compressors are used less than formerly. After each compression, the air enters a coil set in running cold water so that it enters the next stage at room temperature. The rise in temperature for the compression is approximately the same for each of the four stages, to 170° C.

The carbon dioxide may be removed before reaching the compressor, by drawing the air through two towers working in series, filled with coke, down which a solution of caustic soda or caustic potash travels; the air passes up the tower, on the countercurrent principle. The tower packing rests on a false bottom; the liquor accumulates at the base and is circulated to the top of the tower by a small gear pump. Dust is caught at the same time. Another system is to remove the carbon dioxide in the compressed gas between the third and fourth stage.

Before entering the liquefying system, any water in the air must be removed, for water, like carbon dioxide, would deposit as a solid and plug the small pipes or the expansion valves. The amount of water which is brought in by the air is considerable. In a plant making 15 cubic meters of oxygen per hour, taking in 120 cubic meters of air per hour containing 65 per cent of the maximum humidity at 20° C., 193 kilograms [14] of water enter in a six-day period. The greater part of that water is removed by liquefaction as the air from the several cylinders is cooled, and run off before the air enters the next stage; only that con-

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[11] Cooling due to energy consumption in overcoming the attraction between molecules.
[12] 1 cubic meter = 35.31 cubic feet.
[13] Free oxygen means oxygen measured under a pressure of one atmosphere.
[14] One kilogram is 2.2 pounds.

tained in the fourth-stage air, estimated at 1.48 kilograms, needs to be absorbed by a special device. This consists best of a cylindrical vessel with false bottom filled with fused calcium choride sticks; the air travels upward, the liquefied calcium chloride travels down and may be drawn off at intervals. Caustic potash may be used instead, and in that case its liquor can serve in the carbon dioxide removing cylinders.

The compression in the several stages is shown below, and at the same time the volume which at the pressures stated weigh 1 kilogram [14]:

Stages	1	2	3	4
pressure	4.1 atmospheres [15]	14.5	50	200
volume	86 liters	23.35	6.93	1.94

These pressures apply to the starting period; in the running period they are as stated in the table for the first three stages, but the fourth is about the same as the third. Advantage is taken of this fact to send in during the running period so-called low-pressure air (25 to 50 atmospheres) which liquefies easily at the temperature of the liquefier which is very near −191° C.; in this way an important saving in power results.

As a rule the liquefying vessel and the fractionating column are combined, thus avoiding a transference of the liquid. For plants producing more than 15 cubic feet of oxygen per hour, the gas from the fourth stage is precooled by an ammonia refrigerating system; when this is done the water is thereby removed, so that a calcium chloride tower is not needed, and at the same time the air enters the exchanger at a temperature of −30° C., thereby increasing the liquefying capacity of the system considerably.

With a single-column rectifier the wasted gas is 93 per cent nitrogen and 7 per cent oxygen; the yield 66 per cent. With a double-column rectifier, the escaping gas has only 2 per cent oxygen, and the yield is 90 per cent. The latter is shown in the accompanying drawing (Fig. 113).

Two important principles are used; the interchange of heat in double coils, and the rectification of the liquid by means of the columns with shelves. Referring to Figure 113, of the liquefier combined with the double column rectifier, the entering air passes through the inner coils of a double-walled coil system, while the outgoing oxygen and nitrogen surround them. The entering air loses heat to the outgoing gases, and it will be noted from the drawing that the coldest oxygen meets the air already cooled in the upper coils; the warm entering air on the other hand can still lose heat to the oxygen (and nitrogen) which has passed through all the coils and is ready to leave the system. The compressed air thus reaches the coil in the base of the column well precooled; it cools still further in contact with the liquid in the column, and when it reaches the expansion valve, it liquefies readily. This accomplished, the two constituents are separated by permitting the liquid to drop from shelf to shelf, in contact with the rising gas. At each shelf, an interchange takes place; the liquid loses a part of its more-volatile con-

[15] One atmosphere is 14.70 pounds per square inch.

stituent, nitrogen, and robs the gas of a part of its less-volatile con-
stitutent, oxygen, so that the liquid which reaches the lower shelf is
richer in oxygen than the liquid on the shelf just above it. The separa-
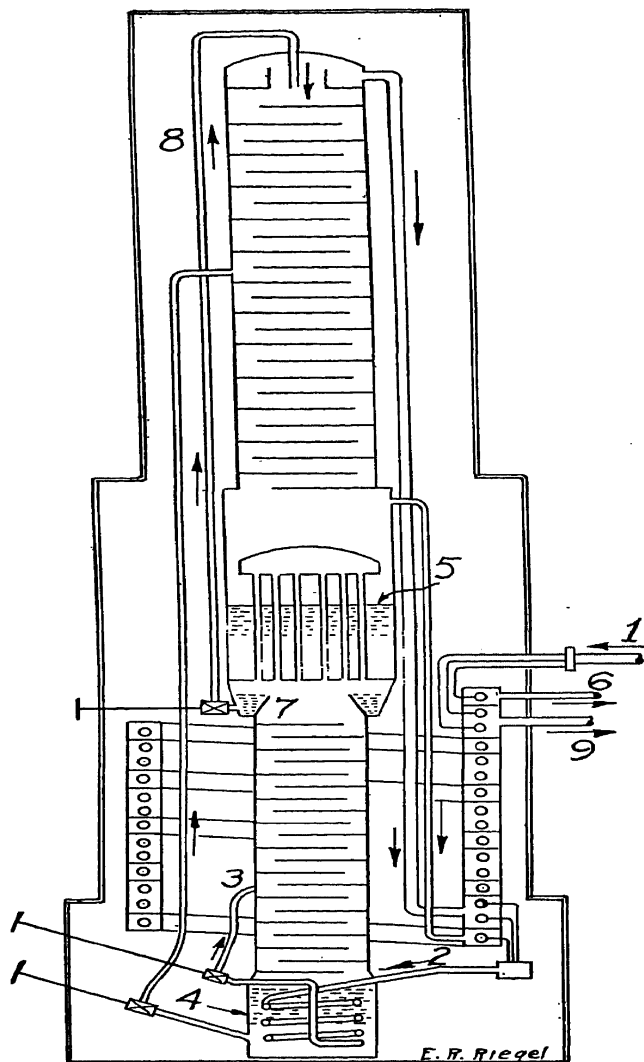
FIGURE 113.—Combined lique-
fier and s e p a r a t o r with
double column (Linde). The
high-pressure air enters at
1, passes through exchanger
coil 2, and is expanded,
reaching the lower column
at 3; liquid rich in oxygen
collects at 4, while the gas
rich in nitrogen reaches the
top of the column, is lique-
fied there and collects at 7;
from here it passes through
a valve into 8 and to the
top of the upper column;
the liquid rich in oxygen
passes from 4 to the middle
of the upper column, loses
its nitrogen on the way
down, so that oxygen col-
lects at 5; the oxygen passes
out here, traverses the ex-
changer and leaves by 6;
the nitrogen gas leaves at
top of still, passes the ex-
changer and leaves at 9.
(Note: The curved dome
over 7 causes the liquefied
n i t r o g e n to drip down
through the outermost tubes
only, so that all of it
reaches collector 7.)

tion is continued in the upper column, as indicated in the illustration.[16]
As the liquid from the lower column at 4 enters the shelves in the upper
column, and descends, it gains in oxygen, while losing nitrogen, until
there is collected at 5 liquid oxygen with only a trace of nitrogen.

[16] Shelves with bells providing liquid seals through which the gases must bubble are in use in
some installations. Plates and bells are of copper.

The oxygen gas is delivered to a three-stage compressor which feeds it to the seamless steel cylinders under a pressure of 2000 pounds to the square inch. A steel container of 40-liter (water) capacity contains at that pressure and at 15° C. 6 cubic meters free oxygen (212 cubic feet). It is delivered to the acetylene torch through a two-way diaphragm reducing valve, at a pressure slightly above atmospheric.[17] Each cylinder is closed by an angle valve which at all times must be free from oil.

Liquid oxygen is also transported in tank cars, or in tanks on trucks and delivered to large users. These users draw some of the liquid oxygen into an intermediate tank from which it can be vaporized, and the gas is then compressed into cylinders. The tank carrying the liquid oxygen is a double wall steel tank with the space between the wall filled with Silocel, and pumped out, until the pressure is between .001 and .020 mm.

Nitrogen. The economical way to utilize liquefied air is to make use of both the oxygen and the nitrogen; the oxygen to fill oxygen cylinders, and the nitrogen which otherwise is lost in four-fold volume, in a special way, such as a reaction. This is rarely realized. As a rule, oxygen plants liquefy air, save the oxygen and waste the nitrogen; while the manufacturer of cyanamid for instance uses the nitrogen and wastes the oxygen. Nitrogen for ammonia fixation is usually made from producer gas.

Argon. In a plant making nitrogen primarily, the argon will first accumulate with the oxygen; this impure oxygen is fed into a very tall column, entering about half-way up. There passes out at the top, through a dephlegmator cooled by liquid nitrogen, 50 per cent argon with nitrogen. This gas enters a second column with a similar dephlegmator at its top, and gives at the base argon with an oxygen impurity, while the nitrogen passes out at the top.[18] The argon is freed of oxygen by passing it over heated copper. Argon is used to some extent to sweep traces of oxygen out of electric light bulbs just before sealing, and in gas-filled lamps.

At atmospheric pressure, argon boils at −185° C., between oxygen and nitrogen.

Neon Signs

Neon and several other rare gases in the atmosphere have been put to work in illuminated signs which allow novel and striking effects; the signs are spoken of collectively under the name "neon signs." These luminous signs consist of slender tubing, such as the chemist has long used in his laboratory, bent into attractive or suitable shapes. They contain a gas at low pressure (12 mm.) through which an electric current of appropriate voltage is constantly passing. This voltage is 6000 to 12,000 volts, the current quantity very small, 25 milliamperes; such current is obtained from the ordinary 120 volt A.C. lighting circuit connected to the primary, taking the high voltage current off the secondary

[17] Ten to 30 pounds for welding. The construction of the reducing valves or regulator is shown in "Das Acetylen," by Vogel, p. 240 (*see under* Acetylene); and in "Oxy-acetylene welding," by S. W. Miller (1916), published by the Industrial Press, New York, on p. 18.
[18] "Die Fluessige Luft," by Kolbe, pages 338 to 343 (Ref. 10).

winding of a transformer. Each sign is furnished by the manufacturer with a transformer which delivers the proper voltage. It is now customary for the sign company to sell service, rather than the sign and equipment, and to tend to the uninterrupted operation of the signs.

The voltage required depends, among other conditions, upon the particular gas or combination of gases used; this difference reflects the ionization potentials [19] of the single gases, listed in Table 32, with the color they produce, and the amount of the gases in the atmosphere.

TABLE 32.—*Properties of the Rare Gases of the Atmosphere, and of Mercury.*

	Ionization voltage 1st electron	Ionization voltage 2nd electron	Color	Parts per million in atmosphere
Helium	24.45	54.12	cream	5
Neon	21.48	40.9	red	15
Argon	15.70	27.82	bluish	9000
Krypton	13.90	26.4	light blue	1
Xenon	12.0	24.25	light blue	0.1
Mercury	10.39	19.0	green-blue	....

Mercury forms part of the gas-vapor system in many tubes, because it carries the current easily, when the tube starts from cold, for example, thanks to its low ionization voltage.

The tubing is 10 to 12 mm.-diameter soft glass tubing, of lead-potash glass. The electrodes are copper, if no mercury is to be part of the tube, or iron, when mercury is used. The area of the electrode was considered an important feature at one time (Georges Claude). Leads sealed in the glass permit connection to outside lines. The electrodes are of sheet metal or woven wire. The tube is shaped over the flame, and its air pumped out through a sealed-in tee; next the current is passed for some time, with alternate exhaustion, in order to remove any trace of air. For a neon sign, neon gas from a one-liter supply flask is admitted by turning a glass-stopcock and reading a mercury gage, until the pressure reads 12 mm.; this requires 2 or 3 seconds. The tube is then sealed off at a previously provided narrowed portion. If the cubical content of the sign is 50 cc., it receives $50 \times 12/760 = 0.8$ cc., so that a one-liter flask suffices for 1250 similar signs. The neon gas in colorless glass tubing gives an intense, very pleasing red. A small amount of krypton might be mixed with the neon, in order to lower the operating voltage. Mercury in clear-glass tubing gives blue, mercury and argon, a better blue. Mercury in amber glass produces green. Other colors will be suggested by the table; still others by combination of colored tubes with certain gases. The smaller the diameter of the tube, the greater the voltage required, but the more luminous the column. The tube is continuous, for lengths totaling not over 10 or 12 feet; the parts not wanted are painted in black, and do not show.

The luminous signs may develop at an increasingly rapid rate if the hoped-for efficiency in the transformation of electrical energy into light

[19] Ionization potential = potential for molecular distances, required for formation of the ion.

is reached. The Mazda lamp furnishes 9 lumens per watt; the neon tube 10 lumens per watt. There is the further consideration that the human eye has a sensitivity quite different for the different colors; for example, 10 per cent of green will seem as intense as 90 per cent of red. George Claude has found that substituting xenon or krypton for argon in the Mazda lamp increases the light efficiency 33 per cent. Improvements in the electrodes for neon signs have been made; thus hollow tubes instead of rods has proved beneficial. Coating the electrode with easily ionized metallic ions [19b] gives good results; thus a tube required 280 volts before coating the electrode and only 70 volts after coating it with cesium.

The difference in ionization potentials may result in hiding certain gases in others, for example, 1 part of krypton in 3 million parts helium is readily detected spectroscopically, but 1 part of helium in 2 parts of argon remains undetected.

The amount of light delivered by a tube depends upon the amperage, not upon the voltage.

The vapor of sodium is used for conducting the current and light production, in a double walled tube to prevent the condensation of the sodium, and with oxide electrodes to maintain a high current density; a special Jena glass (or similar, such as Pyrex Glass) must be employed.[19c]

SULFUR DIOXIDE

Of the more compressible gases, chlorine [20] and ammonia [21] are discussed elsewhere. Sulfur dioxide, SO_2, anhydrous, liquefied under a moderate pressure (2 to 3 atmospheres) at room temperature, is shipped in steel cylinders of 50 or 100 pounds capacity, in 1-ton containers, and in single unit 15-ton car tanks. It is used from such cylinders and tanks in preparing hydroxylamine sulfate, which in turn serves in making dimethylglyoxime, the nickel reagent; for refrigeration, for bleaching, and, increasingly, in petroleum refining (Chapter 24). The boiling point is $-10°$ C.

The burner gas [22] from sulfur (or pyrite), freed from dust, and cooled, is dissolved in water in two towers used in series; the solution from the second tower is elevated to the top of the first tower, where it meets the rich gas. Burner gas with 8 to 12 per cent sulfur dioxide yields a 1 per cent solution. In a third tower this solution is sprayed, at the top, and flows down, while steam is injected at the base of the tower; previously the 1 per cent liquor has been heated in a closed coil laid in the spent liquor from the base of the still. The packing in all the towers may be coke, or special earthenware cylinders. The gas issuing from the third tower is cooled to remove most of its moisture, and is passed up a fourth

[19b] U. S. Patent 2,065,947, and 1,985,855, to Raymond Nauth.
[19c] U. S. Patent 1,984,426, to Marcello Pirani; another patent to the same inventor, also for a sodium lamp, was 1,984,429.
[20] Chapter 5.
[21] Chapters 6, 12, and 14.
[22] Chapter 1.

ower down which concentrated sulfuric acid flows. The dried gas is ompressed in a bronze pump to $2\frac{1}{2}$ atmospheres, which suffices to liquefy it.

Nitrous Oxide. Nitrous oxide, N_2O, is made by heating ammonium litrate to 200° C., in small lots (50 pounds) in aluminum retorts. The gas s cooled in a condenser, washed in a solution of sodium dichromate to remove nitric oxide, in caustic to absorb nitric acid, and in water. Under a pressure of 100 atmospheres it liquefies, in small shipping cylinders for instance; or the gas may be stored in a gas holder. The reaction is $NH_4NO_3 = N_2O + 2H_2O$. Nitrous oxide is used as general anesthetic,[23] usually mixed with oxygen, and sometimes with ether vapor.

Carbon monoxide, CO, is a combustible gas, while carbon dioxide is not; it forms an essential part of water gas, discussed in Chapter 15. The monoxide may be liquified with greater ease than hydrogen, and this has been utilized by Claude in order to separate the two, as discussed in the first part of this chapter.[24] Carbon monoxide is poisonous. Carbon dioxide is presented in Chapter 12.

Acetylene.[25] The two important uses for acetylene are the welding and cutting of steel, and lighting. It is made by the action of water on calcium carbide,[26] a product of the electric furnace:

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

To a great extent, electricity has displaced the acetylene lighting systems in isolated residences and institutions, but for lighthouse purposes, the brilliancy of the acetylene flame has secured its retention in many instances. Carbide is used for miners' lamps in mines free from explosive gases without a screen protection, for instance in rock-salt mines, in gypsum mines, and in certain coal mines. Acetylene is also the raw material which may be made into acetaldehyde, alcohol, acetone, and rubber, as described in Chapters 25 and 39.

In generators which are stationary the construction is usually such that when the drawing of the gas stops, the accumulating new gas depresses the liquid away from the supply of carbide, as indicated in Figure 114. In the miner's lamp an adjustable flow of water passes drop by drop from an upper reservoir to the carbide store below. A third principle is to drop the carbide grains into a store of water. Many forms of generators are portable, and may be moved about the shop; the gas generated may be under high pressure (6 pounds), or low pressure (one-third pound or so). In addition to generators, acetylene tanks furnished by a manufacturer are frequently used; they require no installation; the cost is twice that of the generated gas (leaving out interest on the generator).

In acetylene tanks, the gas is not simply compressed, but dissolved

[23] Chapter 30, *under* Pharmaceuticals.
[24] "The manufacture of hydrogen by partial liquefaction of water gas and coke oven gas," Georges Claude, *Ind. Eng. Chem.*, 14, 1118 (1922).
[25] "Das Acetylen," J. H. Vogel, published in a series of special books on Chemical Technology, by Verlag von Otto Spamer, Leipzig, 1923.
[26] Chapter 17.

in acetone. The reason is that acetylene alone under pressures higher than 2 atmospheres tends to decompose explosively; dissolved in acetone, it may be under pressures of 10 or 15 atmospheres, with safety. The capacity of the ordinary tank (40-liter volume) is about 200 cubic feet of free acetylene. In addition to the acetone, some tanks contain a porous solid filler, such as hardened (by heating) wood charcoal. In order to fill the cylinders, the acetylene gas is dried over fused calcium chloride, compressed in a slow compressor (60 r.p.m.) liberally lubricated with glycerin. The compressor is built to withstand ten times the maximum gage pressure (15 atmospheres). Several cylinders are connected at one time to the compressor and occasionally shut off to allow time for the solution in acetone.
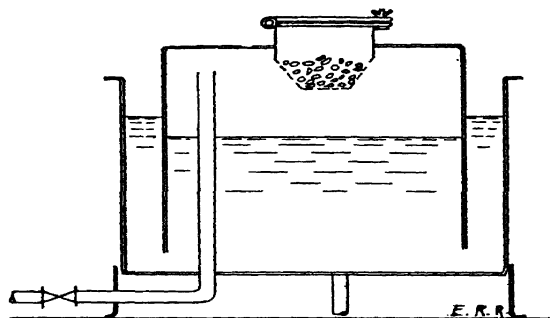
FIGURE 114.—Acetylene generator, stationary type (after Vogel).
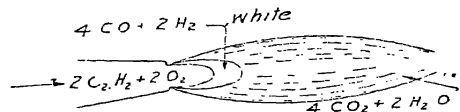
FIGURE 115.—The oxygen acetylene flame (after Vogel).

There are two kinds of welding torches, high pressure and low pressure, differing in important details. Cutting torches differ from welding torches in the following way: in addition to the oxygen and acetylene conduits, which both torches have, the cutting torch receives a stream of oxygen around the flame; it is this oxygen which cuts the steel, by oxidizing it and forcing away the particles of oxide formed; the flame serves merely to attain the oxidizing temperature. The flame in each has an inner brilliant part, whose temperature is estimated at 3000° C.; in the welding torch this is surrounded by a larger envelope into which the air penetrates. The inner portion, which does the welding, is sometimes called the neutral part. (*Compare* Fig. 115.) The use of acetylene is not without danger; the directions and cautions of the manufacturer must be observed.

Other sources, cheaper ones, of acetylene are actively sought; one for example is a natural gas which is pyrolyzed under reduced pressure, or passing a natural gas over a highly heated refractory.[26a]

WELDING BY THE ATOMIC HYDROGEN FLAME

There has been developed a welding torch in which atomic hydrogen, produced by passing hydrogen through an electric arc forming part of

[26a] U. S. Patent 1,983,992.

the torch, furnishes the heat for welding as it combines to form molecular hydrogen. The temperature is as high and higher than that of the electric furnace; it is estimated as between 4000° and 5000° C., so that materials hitherto infusible may be fused. The weld produced may be worked as readily as the original sheet. This flame has the additional advantage that it is non-oxidizing and non-carbonating.[27]

Production. Table 33 gives the production of compressed gases. Vast quantities of these gases processed at once are not reported.

TABLE 33.—*Production of Compressed Gases.**

	1929 Production Cubic Feet	1929 Value Million Dollars	1935 Value Million Dollars
Hydrogen	207,843,000	1.5	1.557
Acetylene	969,543,000	16.5	14.748
Nitrous oxide	109,812	1.2	.946
Sulfur dioxide	17,500,000	1	1.170
Carbon dioxide	137,000,000	7	4.528
Anhydrous ammonia	173,000,000	10	5.674

* Bureau of the Census.

OTHER PATENTS

U. S. Patent 1,850,529, extraction of helium from natural gas, wherein its percentage is comparatively small; 1,881,115 and -6. helium from gaseous mixtures which have boiling points above the critical temperature of helium; 1,772,202, extraction of krypton and xenon from liquid oxygen, by increasing the concentration, then passing through an absorbent for krypton and xenon; 1,892,186, production of argon and neon as by-products in the synthesis of ammonia from atmospheric nitrogen; 1,872,741, production of dry acetylene from calcium carbide and effecting complete hydration of the carbide; 1,794,004, production of acetylene and hydrogen in the electric arc; on isolation of argon, Brit. Patents 218,266 and 226,783 (1924) and U. S. Patent 1,420,802.

Knowles' patents, on electrolysis of water: 1,067,822, apparatus for purifying electrolytic gases by combustion; 1,566,543, electrolytic cell, automatic control of liquid level in electrolytic cell and washing of the gases evolved; 1,485,461, electrolytic cell for production of H_2 and O_2 by electrolysis of water; 1,866,472, electrolytic apparatus for washing gases evolved from a cell by causing them to bubble through water; 1,856,218, electrolytic apparatus using thicker sleeve around the electrode, on the sides not facing the opposite electrode in order to maintain a high purity gas; 1,856,393, temperature controlling system for electrolyte in electrolytic cells; 1,767,292, gas washer for electrolytic apparatus by bubbling gases through chambers containing the washing fluid; 1,767,375, washing gases by bubbling them through chambers containing the washing fluid; 1,821,018, electrolytic apparatus for electrolysis of liquids for production of gases. 2,057,908, on a luminous tube, to Raymond Nauth, the tube has a small heated pocket for mercury; 1,988,459, luminous discharge tube system.

PROBLEMS

1. In the steam-iron process for hydrogen, the retorts as given in the text produce 3500 cu. ft. per hour. Over the day, how many hours are all the retorts in actual operation of hydrogen? Disregard purging period. If 3 times the amount of necessary steam is taken, what is its weight?

2. In the installation of 306 Knowles' cells given in the text, let the current efficiency be 100 per cent, and let the operating voltage be 2. What is the energy efficiency? Compare Chapters 5 and 18. For the production of hydrogen gas as specified, how much distilled water will be required?

[27] "Flames of atomic hydrogen," Irving Langmuir, *Ind. Eng. Chem.*, **19,** 667 (1927); or *General Electric Review*, **29,** 153 and 160 (1926).

3. Let the "parts per million" for the rare gases in the atmosphere represent volumes. How many cu. ft. of air will be required in order to prepare 1 liter of each of the rare gases? The first operation for liquid oxygen has a 90 per cent yield; assume that its rare gas content is the same as in the original air. The recovery on from there may be taken as 80 per cent.

4. An acetylene generator receives a charge of 250 pounds of calcium carbide, 75 per cent CaC_2. What is the volume of acetylene gas which may be generated, measured at ordinary temperature and pressure?

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A number of chemical industries depend upon the existence of minute plant organisms, so small that they are visible only under a high-power microscope; they are therefore called micro-organisms. Under the proper conditions, they grow at enormous speed; they have the power to consume (apparently) one substance and to produce another, and it is this function which makes them valuable. In these industries, the chemist joins hands with the bacteriologist.

Chapter 20

Processes Based on the Activity of Yeasts and Bacteria

From time immemorial, one of the processes which depends upon the existence and growth of micro-organisms has been practiced, namely, that of alcoholic fermentation of grape juice and fruit juices, but the exact nature of the process remained a mystery until Louis Pasteur discovered, isolated, and classified the several kinds of organisms. He succeeded in demonstrating that fermentation and bacterial disturbances in general were not due to spontaneously generated plant organisms, but to organisms which already existed elsewhere and which were carried in by air currents,[1] on the skin of the fruit, or in other ways. At the same time, the nature of the festering of wounds became clear; as a result, the modern science of antiseptic treatment was born.

The transformation of certain sugars, the monosaccharides, such as glucose and fructose, into alcohol, is brought about by yeast; carbon dioxide is evolved profusely at the same time, so that the liquid seems to boil.[2] The formation of lactic acid is due to a bacterium. The place of these organisms in the complete group will be clearer from some general considerations.

Yeasts, bacteria, and molds are fungi, vegetable growths. Yeasts multiply by budding, with or without spore formation; bacteria multiply by division or fission, in rare cases by spores. Yeasts show a definite nucleus under the microscope, whereas bacteria do not. Yeasts are commonly egg-shaped, and about 0.01 mm. in diameter; bacteria are long or short rods,[3] comma-shaped, and in general, smaller than the yeasts (about one-tenth the size of yeasts). Bacteria and yeasts differ from molds in that the former two are unicellular, while the latter is multicellular. Molds multiply by sporation. Protozoa are the lowest form of animal life; they are one-celled, and are found in ditch water (amoeba).

The yeast cell contains complex organic substances called enzymes, whose characteristic is that they can catalyze a chemical reaction; the

[1] Pasteur had to ascend the Alps many hundreds of feet above human habitation, before he could find air which would not contaminate his test solution (veal broth).

[2] Hence the name fermentation, from the Latin word *fervere*, to boil.

[3] The long rods are bacilli; the short ones, bacteria proper.

reaction they catalyze is the same as the one the cell as a whole catalyzes. As a rule, the yeast contains a number of different kinds of enzymes. In industrial operations, the enzyme is not isolated; the cell is cultivated and used. For growth, the alcoholic ferment requires sugars, a small amount of mineral salts, phosphates, and nitrogenous matter; the effort of the manufacturer is not to grow yeast, for 1 gram of pure yeast requires 1 gram of sugar, and hence there would be no production of alcohol, but rather to produce just enough yeast to catalyze the alcohol-forming reaction. Some growth takes place, but the main part of the conversion is due to the action of the formed cells.

Yeasts and bacteria grow best and work best at definite temperatures which vary with the several organisms, but which lie not far from the room temperature, perhaps between 5° and 40° C.; 60° is fatal to most of them. In general the working range for bacteria is narrower than for yeasts. These microscopic plants are carried about by every gust of wind, so that it is difficult to keep any one batch of liquid free from contamination. In order to control the action, all organisms already in the material are destroyed by a preliminary heating, called sterilization; after cooling, a pure strain of the desired organism, grown under protection (aseptic conditions), is introduced; this is called inoculation, or seeding. Not only the temperature, but the acidity has an effect on the activity (and growth) of the organisms; alcoholic ferments work well in an acid medium, while most of the bacteria are inactive; on the other hand, too high a concentration of alcohol will destroy the yeast itself. In order to grow, yeast requires air; it causes fermentation best out of contact with air.

INDUSTRIAL ALCOHOL

Fruit juices are fermented and distilled, to concentrate the alcohol formed, for the production of potable spirits whose value lies largely in the flavor characteristic of the particular fruit used; the finished liquor purposely betrays the origin. It is different with industrial alcohol, for this must be as near chemically pure as possible, and must bear no marks of the original material. Industrial alcohol is ethyl alcohol, 95 per cent. The sources for industrial alcohol must be cheap, otherwise the uses will be limited; preferably by-products of other industries are sought. In the United States and in England, the chief raw materials are cane-sugar molasses and beet-sugar molasses; in France, sugar beets, and beet-sugar molasses; in Germany, potatoes, lately also beet-sugar molasses. Any starchy material may be used, such as corn [4] and other grains; these are, however, generally more valuable for food purposes. The liquor from the sulfite wood-pulp digester has been made into alcohol, and wood and sawdust have been used in experimental plants. In order to prevent the diversion of industrial alcohol to potable alcohol

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[4] By using damaged corn, a fairly cheap raw material may be obtained; 1 ton of corn (33 bushels) yields 90 gallons of 95 per cent alcohol; at half the normal price the raw material would be about 20 cents per gallon. For other prices, *see* further.
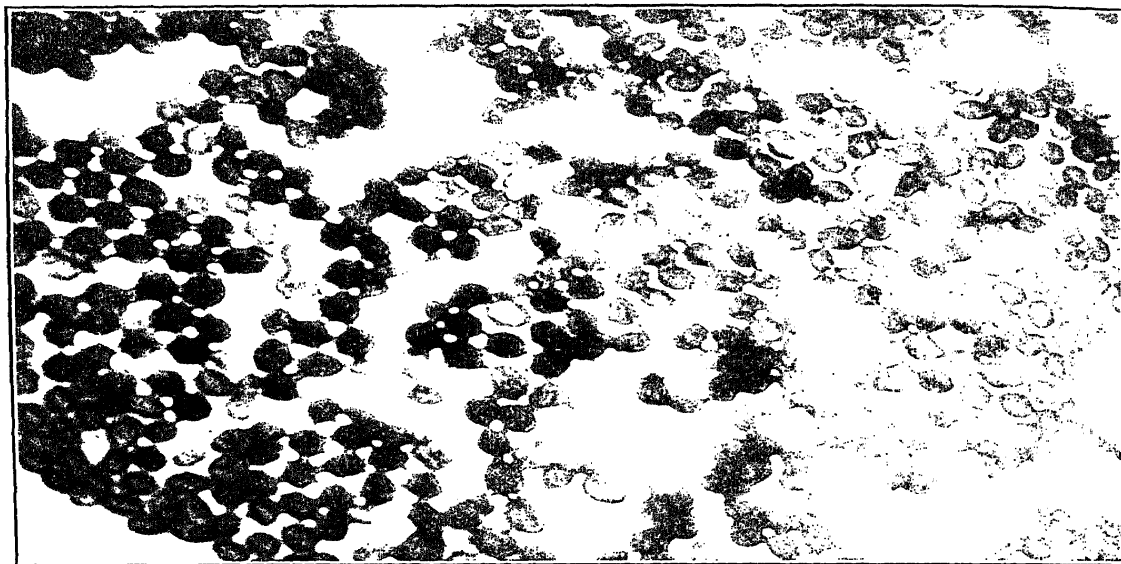
FIGURE 116.—Yeast cells, magnified 300 times. The light cells are the disintegrating ones; the dark cells the growing ones. The inter-connection between mother and daughter cells is shown in the lower left; in several places, a cell with bud formation is visible.
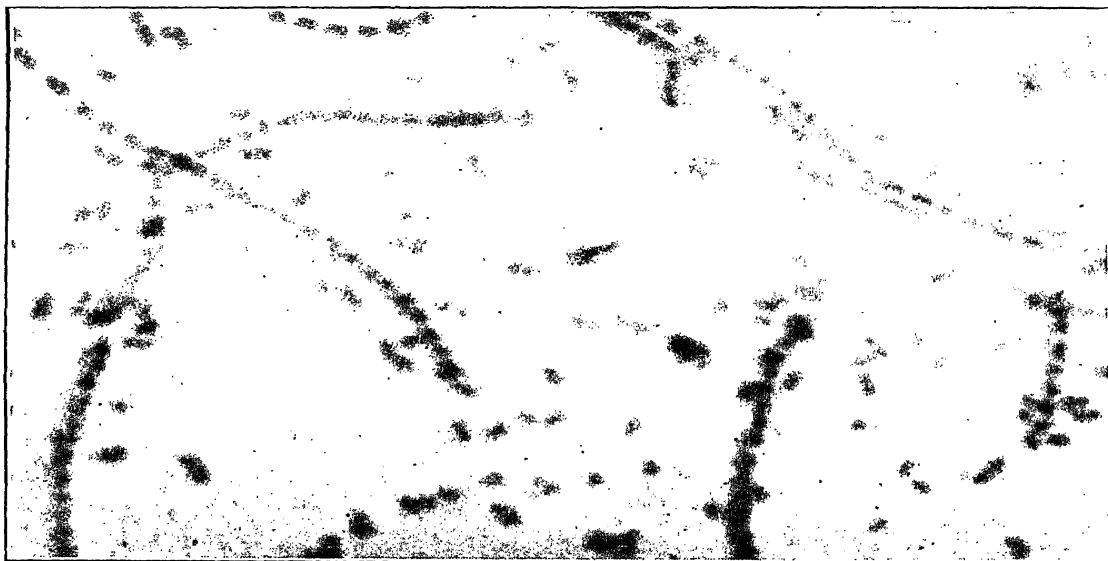
FIGURE 117.—Bacterium lactis acidi, used for the production of buttermilk, magnified 1800 times.

uses, it is denatured by adding some material which is not easily separated by any physical or chemical process and which renders denatured alcohol unfit for use as a beverage. A number of different formulas are authorized by the Government so that the industrial user may select the particular formula which will have the least effect upon his particular process (*see* further).

For molasses, the process is essentially a fermentation, followed by distillations. For potatoes and grains, the starch must first be rendered soluble by malting; the water extract containing the dissolved starch, the wort, is then fermented, and the fermented solution distilled.

Alcohol from Molasses. Molasses is well suited for the production of alcohol (ethyl alcohol C_2H_5OH) for it contains sugar[5] in a form which permits direct fermentation by yeast; the absence of hulls or peels also simplifies the process. Molasses is the final mother syrup in the crystallization of table sugar, or crystal sugar; 15 to 20 per cent of the sugar in the sugar beet, or cane, cannot be crystallized without special installations, because the accumulated non-sugars prevent crystallization.[6] Molasses from cane sugar differs somewhat from the beet sugar molasses, as shown in Table 34.[7]

TABLE 34.—*Analysis of Typical Cane and Beet Molasses.*

	Cane molasses	Beet molasses
	Per cent	
Water	20	20
Sucrose	30	50
Raffinose	0	present
Invert sugar	32	trace
Ash	6	10
Organic non-sugars	12	20

Sucrose is the crystal sugar, and is the same substance whether made from the sugar cane or the sugar beet; it is a disaccharide $C_{12}H_{22}O_{11}$. It is converted by invertase, an enzyme present in the yeast, into two molecules of monosaccharides, with the addition of water:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
sucrose (d)   d-glucose   l-fructose
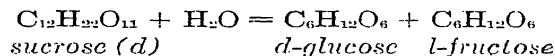
The monosaccharides, glucose and fructose, are attacked by the enzyme zymase, the most important enzyme in the yeast, and are changed into alcohol and carbon dioxide. Invert sugar consists of equal parts of d-glucose and l-fructose.

The molasses is received at the alcohol plant in the form of a thick, dark syrup, transported in tankboats holding from 1 to 2 million gallons; another method which is less common is to concentrate the molasses in a vacuum pan, and to run the concentrate into cast-iron water-cooled

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[5] The chemist distinguishes many kinds of sugars; sucrose, glucose, and fructose are discussed in this section; raffinose is a tri-saccharide, with C_{18}; *see* Chapter 23.

[6] The limit is 60 parts sugar to 40 parts non-sugars.

[7] *Chem. Met. Eng.*, **16**, 437 (1917).

molds, where it solidifies to a loaf. The mold is previously lined with paper which sticks to the loaf and protects it against moisture absorption. Wooden casks are now rarely used.

The molasses is diluted with enough water to produce a solution or "mash" containing about 10 per cent sugar. A nutritive solution may be added to the mash after dilution, providing there is insufficient yeast food in the molasses. With cane molasses a small amount of sulfuric acid is added (about one gallon of concentrated acid to 4000 gallons mash) in order to produce a slight acidity which retards any bacterial action. With beet molasses it is necessary first to neutralize the mash and then add sulfuric acid as in the case of cane molasses. The yeast requires a slightly acid solution for its most vigorous growth. If desired, the bacteria in the original molasses may be killed by sterilization, in which case it is only necessary to be sure that the mash is not alkaline. Cane molasses requires no acid if sterilized.

Previous to this mashing, the laboratory has prepared yeast in sufficient quantity to inoculate the mash; about 5 per cent in volume is required for proper fermentation. The mash is brought to the proper temperature and the yeast added. Considerable heat is evolved during fermentation, causing the temperature of the mash to rise. This should be controlled so that the final temperature never goes above 100° F. (37.8° C.). If there is no cooling available, such as coils immersed in the fermenting vats, it is necessary to cool the mash before adding the yeast. The proper starting temperature can only be determined by experimenting but it is usually around 70° F. (21° C.). The time required for complete fermentation is about three days.

In about three hours' time after adding the yeast the evolution of carbon dioxide can be readily observed. The amount of this gas gradually increases until at the end of 24 hours the entire mash appears to boil. During the early stages of fermentation the yeast grows and then proceeds rapidly to convert the glucose and other monosaccharides into alcohol. At the same time, the enzyme invertase in the yeast is converting the sucrose to monosaccharides.

The fermentation vats are commonly made of steel but may be made of any material which can be readily sterilized. Wooden vats were used in some of the older installations. The yeast tanks, like the fermenting vats, must be constructed of material which can be easily cleaned and sterilized; best of enameled iron.

The principal reaction during fermentation is

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$
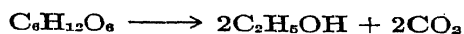
Other products formed are higher alcohols, called fusel oil (of which iso-amyl alcohol is the principal one), glycerin, and a small amount of organic acids.

The carbon dioxide evolved from the fermentation may be collected by covering the fermenters and piping the gas away. The gas is usually

purified by scrubbing with water to recover the alcohol contained therein and then passing the gas through an absorbing material such as charcoal to remove the odors. It is then compressed and bottled in steel cylinders as liquid carbon dioxide or made into the solid.[8]

The product of the fermentation is a weak alcohol, which must be concentrated; this is followed by rectification. The final product is 95 per cent alcohol. The yield is about 0.4 gallon (U.S.) per gallon of molasses, analyzing as shown in Table 34, and this represents about 90 per cent of the sugar converted to alcohol. The loss is due to alcohol vapors[9] which escape from the fermentation vat, and to side fermentations which produce other substances than alcohol. The residue from the distillation is a more or less clear liquid which may be concentrated and evaporated to dryness for the potassium salts which it contains.[10] The yeast remains in the liquor and is destroyed. In the larger plants, it is customary to run a smaller fermentation plant expressly to obtain yeast in pure cultures; the procedure is somewhat different from the main fermentation. The species of yeast best suited is taken from the surface of the sugar cane.

Alcohol from Grain and Potatoes. The method of making alcohol from grain and potatoes includes the fermentation described under molasses, but in addition a preliminary treatment designed to dissolve the starch, the source of alcohol in this case, and to hydrolyze it, by enzymes, to a form of sugar which can be attacked by yeast.

The process as practiced with potatoes may serve as illustration. Potatoes contain 15 per cent starch, which is insoluble in water, and moreover surrounded by pulp. The potatoes are placed in a cooker with a conical bottom terminating in a valve; 60-pound steam is sent in, for a period of perhaps one hour, after which the cooker is blown empty. The pulp so obtained is made up with water, and contains the starch free and in solution. After screening off the skins, the suspension is mixed with malt[11] which by virtue of its diastase (an enzyme) content changes the starch into a disaccharide, maltose. After the proper period, the maltose solution is drawn off from the insoluble, settled portion (washed twice), and is ready for fermentation; this solution is the wort. The suspension as a whole, after the malting period, may be fermented and subsequently distilled; the steps are the same as with the clarified wort, but special distilling apparatus must be used.

Malt is made in a preliminary operation, by the controlled (partial) germination of barley. The barley is first steeped in cold water, then heaped on the floor in the air, and occasionally turned over; the temperature rises, oxygen is absorbed, and carbon dioxide is given off. The germ within the barley, the plumule or acrospire, grows by this process,

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[8] Chapter 12.

[9] In the installation with carbon dioxide recovery, this alcohol is saved.

[10] The still residue is first concentrated at 32° Bé., and this thick liquid supports its own combustion in special furnaces; the ash contains the potassium. The primary purpose of the operation is to dispose of the enormous amount of waste liquor. *See* Chapter 8.

[11] The proportions are 2 pounds of malt to 100 pounds potatoes; for corn (maize), 8 pounds of malt to 100 pounds of corn. One ton potatoes gives 100 to 120 United States gallons.

and contains the desired soluble ferment, the diastase. Such malt, crushed between rollers and mixed with some water, is the agent which alters the dissolved starch to the sugar, maltose. About four-fifths of the starch in the potato is obtained in the wort, as maltose solution.

Instead of malt, mineral acids may be used.

The dilute alcohol from the fermenting vats (7 to 12 per cent) is concentrated by distillation in an apparatus with continuous operation.

CONCENTRATION AND RECTIFICATION IN A SINGLE, CONTINUOUS SYSTEM

One of the earliest and best-known methods for the continuous distillation and rectification of the fermented liquor, with complete separation and purification of the 95 per cent alcohol and by-products, is that of Emile Guillaume.[12] This process has been modified and improved in the intervening years, and others invented, but inasmuch as it illustrates principles common to all, it will be described here.

The Guillaume Process. The essential parts of the Guillaume process are shown in Figure 118. The apparatus consists of a boiler (not shown), the rectifying column A, the purifying still B, a vessel C to maintain a given alcoholic content, a distilling column D for exhausting the charge, the alcohol still E, dephlegmators, condensers, and auxiliary apparatus. There is no connection between still B and column D; a solid metal plate (21) separates them. They are superimposed merely for convenience.

The crude alcoholic vapor from the boiler enters the internal drum, at 2, in the bottom of still A, merely passing through on its way to still B through pipe 3. This drum is the source of heat in A.

All of the boiler vapor arrives in B, it is merely somewhat cooler, and partly liquefied. A portion travels down the plates of this column, to meet an entering supply of live steam (entering at 38). The condensate loses aldehydes and all volatile impurities, and reaches the bottom of B. The condensate is almost pure. It is conveyed through pipe 4 to the storage vessel C.

In B, the volatile impurities travel upward, being at the same time fractionated. A regulated stream of water is added at 29, in order to dilute the alcohol sufficiently to hold it back. The fusel oil is drawn off at 31, to be fractionated further in a separate apparatus; this fraction contains amyl alcohol, amyl valerate, ethyl acetate, ethyl isovalerate, ethyl butyrate, and similar bodies. Escaping condensation in the dephlegmator G, the aldehydes and formate esters pass into condenser J and from there, now liquid, to receiving vessels.

By adding water at 29, the various esters and higher alcohols can be distilled away from the alcohol without any great amount of alcohol distilling. This is because the esters and higher alcohols are comparatively insoluble in water and do not suffer a reduction of vapor tension due to water admixture as does ethyl alcohol.

[12] U. S. Patent 887,793 (1902).

The purified, weak alcohol in *C* is delivered at a continuous rate to the still *D*, where it travels over the plates downward, meeting live steam which enters the column *D* at **39**. There passes out of *D* to the open column **41** a vapor containing all the alcohol and considerable water; it reaches column *E* where it is condensed, fractionated and concentrated

FIGURE 118.—The Guillaume process, for the concentration and rectification by continuous operation of the beer from the fermenting vats. *A*, rectifying still; *B*, purifying still; *D*, weak alcohol still; **41**, open still surmounted by alcohol column. *C*, storage vessel for hot hydrous alcohol. (*See* text for o t h e r parts.)
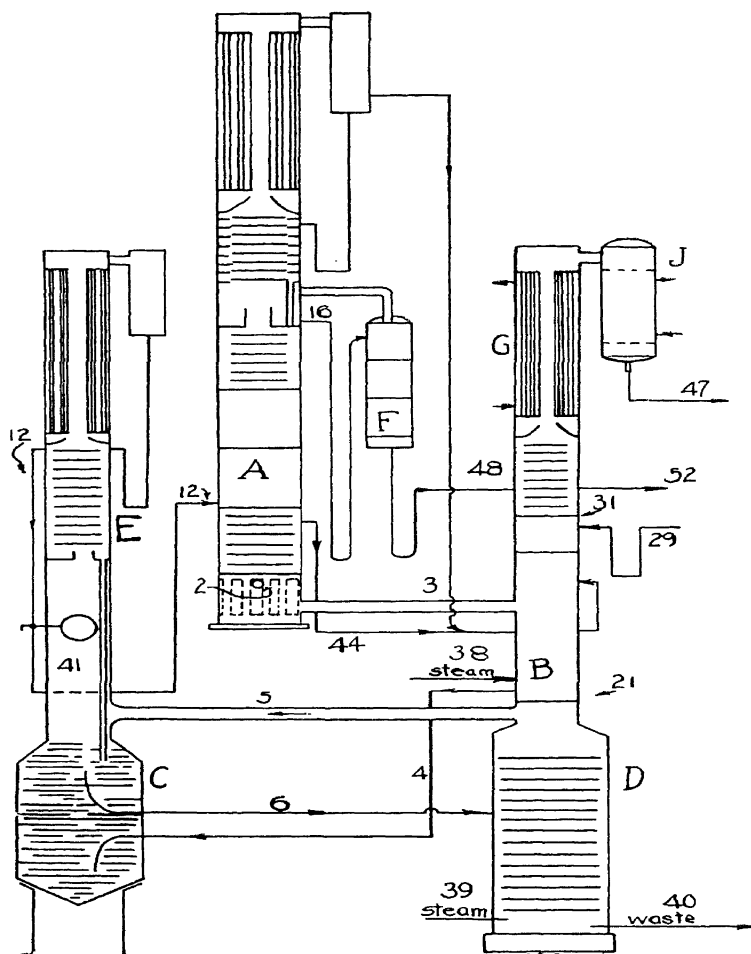
in the usual way. The product from E is 86 per cent alcohol, still purer than when it entered vessel *C*, for a small amount of amyl alcohol is removed from the lower plates and sent to **48**; it leaves *E* at the upper plate through line **12** leading to the bottom of still *A*, where the final rectification to the full strength takes place. A weak residue passes out of *A* through pipe **44** and is returned to the system at still *B*. The strong alcohol leaves *A* through pipe **16**. It is passed through a supplementary

column for a final purification of such esters as were formed during the process of distillation, through oxidation and esterification.

The flow of the various liquids is regulated by valves and a control mechanism located in open still 41, and depends upon the temperature of the vapors.

In one of the more recent continuous processes for the production of 95 per cent alcohol, the addition of liquid water is avoided, only water in the form of steam is injected. The proper operation is insured by the temperature at a selected point, about two-thirds of the way up, 85° C., under which condition the vapor passing out at the top of the still will be 95 to 96 per cent alcohol. Should the temperature go higher, a larger amount of condensate from the condenser above the still is returned to the still; should it go lower, the amount of the same cold liquid is decreased.[13]

The concentration of aqueous alcohol is possible because when it is vaporized, the vapor is richer in alcohol than the liquid from which it rises (*see* Fig. 119). There is at each plate of the still an enrichment
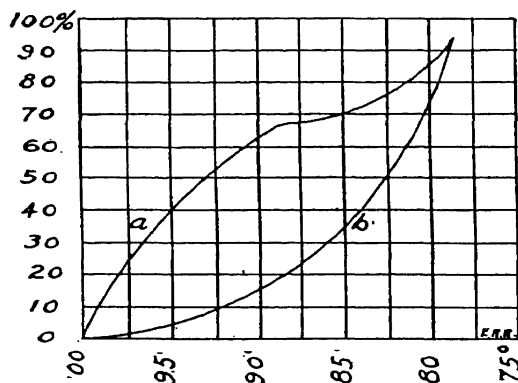
FIGURE 119.—Difference in composition between the vapor and the liquid for alcohol-water mixtures. Abscissæ, boiling temperatures; ordinates, percentages of alcohol in *a*, the vapor; *b*, the liquid. Example: At 90° C., the liquor has 16% alcohol, but the vapor rising from it has 62%.

of the vapor, which rises to the next plate, there to gain again in alcohol, while the liquid descends, to meet on the lower plate a leaner vapor to which it loses alcohol. The paths of vapor and liquid are countercurrent. Pure alcohol (ethyl alcohol C_2H_5OH) boils at 78.5° C., water at 100° C.; starting with an aqueous alcohol, the gain in alcohol in the vapor continues until 97.2 per cent by volume is reached; beyond that the vapor no longer differs from the liquid from which it rises (constant-boiling mixture, with boiling point 78.174° C.); for this reason, 97.2 per cent alcohol is the highest strength obtainable by distillation alone. Industrial alcohol contains 95 per cent alcohol; the remainder is water.

"100 U. S. proof" contains 50 per cent alcohol; "200 proof" is pure alcohol. The "100 British proof" is slightly stronger than the 100 U. S. proof. Alcohol of 100 U. S. proof will burn when touched with a match.

Synthetic ethyl alcohol is made from ethylene or from acetylene (Chapters 24 and 25).

[13] U. S. Patent 1,835,848.

Cost and Uses of Industrial Alcohol

Alcohol has so many uses in the industries and in the arts that it may be said to be indispensable. This is reflected in its production figures, which are large; for 1935, (as reported to the Bureau of Internal Revenue) 193,218,597 gallons in terms of proof gallons, that is, 100 per cent ethyl alcohol. In 1931, the U. S. production was 75,731,000 gallons, in terms of 100 per cent alcohol. In 1929, the production was 106,960,458 gallons, with an average quotation of 48 cents a gallon; in 1935, the value of the ethyl alcohol (and a small amount of "other alcohols"), was $31,382,286. Some of the uses depend upon its chemical nature, and no other substance could be substituted; chief among these is the manufacture of ether.[14] Other chemicals are made from alcohol, although they could be made from other raw materials; chloroform is an example. The perfume industry makes use of the solvent power of alcohol for essential oils; no suitable substitute is known. Certain flavoring extracts (vanilla) similarly require alcohol as solvent, as do furthermore the lacquer, Celluloid, smokeless powder, and other industries. Alcohol serves also as a fuel, in lamps and burners, liquid, and in the form of "solidified alcohol" [15] or as motor fuel in internal combustion motors; this latter use is susceptible of considerable development which will depend upon the supply of crude oil and gasoline, and on the price of alcohol.

The cost of alcohol depends upon the cost of the raw material, on the cost of fuel,[16] and on the efficiency of the fermentation. If molasses costs 10 cents a gallon, which would be high, and 2½ gallons of molasses are required to make 1 gallon of alcohol, the usual yield, then the latter must amount to 25 cents for raw material alone. The cost of converting molasses into alcohol is about 4 cents per gallon deposited in storage tanks. There is an additional cost of about 4 cents for overhead and for labor and materials required in denaturing, barreling, shipping, etc. The selling price for alcohol is in the neighborhood of 40 cents per United States gallon. In Germany the price is less, because of a state subsidy. It has been estimated that with wood waste as a source, a much lower cost might be reached.[17]

In nearly all countries, ethyl alcohol for industrial purposes may be obtained tax-free; in order to prevent the diversion of such alcohol to beverage uses, certain distasteful, even poisonous substances are added. In the United States, there are two classes of denatured alcohol: Completely denatured, which may be sold without a permit, and especially

[14] Chapter 30.

[15] U. S. Patent 1,208,265, to C. Baskerville. The proportions and ingredients are 10 to 15 per cent saturated calcium acetate solution, 85 to 90 per cent industrial alcohol, 0.5 to 1.0 per cent stearic acid.

[16] The fuel required is estimated at 11 pounds of coal per gallon.

[17] The residue from the wood used would be the fuel, involving no additional cost. "Wood waste as a source of ethyl alcohol," G. H. Tomlinson, *Chem. Met. Eng.*, **19**, 552 (1918); *see also Chem. Met. Eng.*, **21**, 558 (1919), and the chapter on the manufacture of alcohol from waste wood and sulfite cellulose liquor in "Industrial Alcohol," by J. G. McIntosh, revised by H. S. Stocks, published 1923 by Scott, Greenwood and Son, London. It would seem that the cellulose proper is not the source of alcohol; a residue of 65 per cent of the wood used is left, corresponding closely to the cellulose present; *compare* p. 183, in the book of McIntosh and Stocks. Soft woods give 25 gallons per ton, hard woods only 10. *Note furthermore* the Bergius process, chapter 16.

denatured alcohol. The standard denatured alcohol for radiators contains, to 100 parts 80 per cent ethyl alcohol, 5 of isopropanol, 0.75 of aldehol A, 0.75 of alcotate, 0.25 of terpineol (1933). The quotation for completely denatured alcohol, *Formula No. I,* is 44.3 cents a gallon in drum lots (54 gallons), in June, 1937. Aldehol is the name given a liquid made by blowing air through boiling kerosene. There are over 30 specially denatured alcohol formulas suitable for specific purposes. These are sold to manufacturers who may select denaturing materials which have no effect upon their particular processes.

<center>BREWING INDUSTRY</center>

The manufacture of beer will be described for a brewery of small or medium size (40 to 100 barrels per day, 1 barrel = 31 gallons).

The preparation of malt is given under industrial alcohol; the brewer may prepare his own malt, or, as is common, buy it from the malt house; it is delivered in trucks. The malt is placed in the "mash tuns," large iron vessels with agitators, and "mashed," that is, made up with water at 160° F. (60° C.). The purpose of mashing is to extract from the malt the saccharine substances, dextrine, and to change the unconverted starch into sugars. By means of steam coils in the tun, the heat is gradually raised over a period of 2 to 3 hours to 180° F. (82.2° C.). The starch and diastase extract is passed through a false bottom to the "brewer's kettle," a copper boiler, situated on a lower floor. The residue in the tun is made up with water again, and this extract added to the first ("sparging"). The liquid at this stage is called the "wort."

In the copper boiler, corn sugar and dried hops are added; 5 pounds of sugar and one-half pound of hops to each barrel of wort. By means of a copper steam coil, or steam jacket, the wort is brought to a boil. After boiling for one-half hour, another, but smaller amount of hops is added. A little later, the steam is shut off and the contents left at rest; if the lower part of the settled liquid is drawn off, the remainder will be a brilliantly clear, brown-colored liquid. It is sent to a long rectangular tank about 3 feet deep (or other coolers), and allowed to cool. The object of boiling is to concentrate the wort, to extract the hops, and to coagulate albuminous substances and cause them to settle with any unconverted starch.

The clear hopped wort from the cooler passes to the fermentation vats, which may be made of wood, aluminum, or glass-lined steel (vitrified enamel). They may be circular, or square in cross section. The fermentation is carried on at 68° F. (20° C.). Yeast is added at the rate of ¼ to 1 pound per barrel of wort. The fermentation begins after some time, and progresses slowly; should it go too fast, the liquid is cooled by cooling coils, in order to retard the action; after 5 to 7 days it is complete. As the action progresses, the amount of yeast increases, and is skimmed off. It is used over again, provided a test culture shows it to be pure. If the fermenting action is too slow, more yeast is added. The greatest care

must be taken to exclude other organisms, and this leads to a cleanliness which makes a brewery a show place. The material which ferments is, among other things, the corn sugar, so that by regulating its amount, the amount of alcohol in the finished beer may be largely controlled. The 1933 law allows 4 per cent by volume, or 3.2 per cent by weight.

When the fermentation is considered complete, the liquor is placed in resting tuns. It then passes after one or more days to a filtration vessel, in which "Filter Cel" or a similar filter aid is added, stirred in, in order to furnish points of attachment for the colloidal substances and the dead yeast cell, preparatory to filtration. Filter leaves are immersed in the beer, and the clear beer is drawn out, free from any yeast, by a pump; it is delivered to storage casks in the cellar. It remains in storage a minimum of 4 days, but, better, for weeks or months, at the temperature of $40°$ F. ($4.4°$ C.). The beer improves with the period of storage. It is carbonated in a special carbonating tank, by passing in sterile carbon dioxide under pressure.

For shipment, the beer is kegged or bottled; if the latter, the bottles are pasteurized at $180°$ F. after capping.

ABSOLUTE ALCOHOL ON COMMERCIAL SCALE

In addition to industrial alcohol, there is now on the market, in drum lots and carload lots, 100 per cent ethyl alcohol, called absolute alcohol. This material has properties of miscibilities which industrial alcohol does not possess. In making a motor fuel from gasoline and alcohol, 95 per cent alcohol may be used, it is true, but only by introducing a third component, such as benzene (= benzol), ether, or tetralin (Chapter 25). Without this third component, industrial alcohol does not mix with gasoline. Absolute alcohol does not require a blending agent; it is miscible with gasoline in all proportions.

Such blended motor fuels are of no economic interest in the United States, where gasoline is abundant and cheap, but they are important in countries which must import their petroleum products. Even in the United States there have been proposals to add 5 per cent alcohol to gasoline, as a "Farm relief" measure; to date, they have come to naught.

A second important demand for absolute alcohol comes from the lacquer industry, in which it is a valuable solvent.

Thanks to several continuous methods, absolute alcohol is obtainable at a very reasonable price.

The Keyes Process. In the process patented by Donald B. Keyes [18] advantage is taken of the fact that on addition of a third constituent such as benzene (= benzol) to the alcohol and water present in 95 per cent alcohol, a three-constituent mixture, or ternary mixture, with a constant, low boiling point, is formed, and this mixture may be driven out, leaving the greater part of the alcohol free from water in the lower part of the still. The benzene as well as the alcohol in the ternary mixture

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[18] U. S. Patent 1,830,469.

may be recovered completely by suitable secondary operations. This is facilitated by the interesting fact that on cooling, the ternary mixture condenses to form two immiscible layers, the upper containing most of the benzene; the lower, most of the alcohol. By means of a separator, these two layers are divided, and sent to different rectifying stills.

The ternary constant boiling mixture boils at 65° C., and contains

Alcohol	....	18.5% by weight
Benzene	....	74.1%
Water	....	7.4%

It boils considerably lower than pure, dehydrated alcohol (78.5° C.).
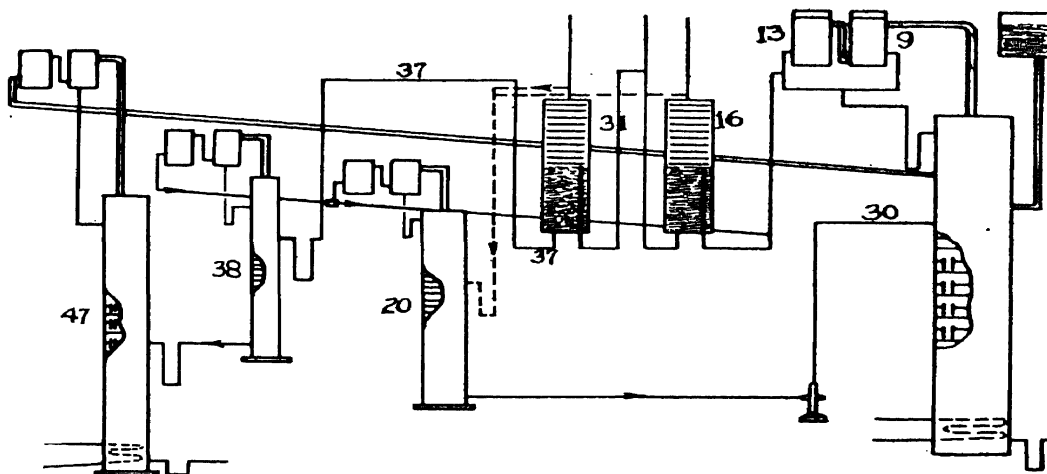
FIGURE 120.—The Keyes process for absolute alcohol. At the right, the main still, giving absolute alcohol at its base. 20, benzene column; 38, alcohol rectifying column; 47, alcohol recovery column. (For other parts, *see* text.)

On condensing, this ternary mixture forms two separate, immiscible layers, which have, at 28° C., the following composition:

	Upper layer	Lower layer
Alcohol	11.6% by weight	51.3% by weight
Benzene	85.6%	8.1%
Water	2.8%	40.6%

Of the total, the upper layer is 84.7 per cent, the lower, 15.3 per cent, all by weight.

The procedure will be described in greater detail, with the aid of Figure 120. Industrial alcohol is fed into a 40-plate still, the main still, at the tenth plate from the top. Benzene is introduced, in an amount sufficient to form the constant boiling mixture with all of the water present. Fractionation takes place, the liquid becoming richer in alcohol as it descends, while the vapors of the ternary mixture pass out at the top of

the still. These vapors reach dephlegmator 9, which is kept at 65° C., so that any excess alcohol vapor is condensed and runs back to the still; they continue to condenser 13, where they liquefy, and from there run into separator 16, where the two layers form. Heat is supplied to the still by a steam coil; the temperature at the base of the still is 79° C. The absolute alcohol is drawn off at that point, cooled and stored.

The upper or benzene layer in 16 passes to the benzene column, 20, heated by a steam coil (indirect heat). There rises the ternary constant boiling mixture, consuming all the alcohol and water, but leaving the excess benzene. This latter is drawn off, cooled, and is pumped back into the main still through pipe 30.

The lower layer in 16, which might be called the water layer, passes to scrubber 31. Water is run in, and two layers form again; the upper layer is run to column 20, where its benzene is abstracted. The lower water layer goes through pipe 37 to column 38, heated again by a closed steam coil. The ternary mixture rises, this time exhausting the benzene, leaving the excess alcohol and water in the still. The vapors are dephlegmated and then condensed, and pass to 16. From the bottom of 38, a 30 per cent alcohol is drawn and sent to the alcohol recovery column 47, which sends out at its top in vapor form 95 per cent alcohol, and allows removal at its base of the water. The heat for this column is also indirect.

This process has been in successful operation for several years.[19]

Other substances instead of benzene may be used as the third constituent in the ternary mixture which is essential to this process; for example, ethyl acetate, carbon tetrachloride, or hexane.

Another process which uses a water-immiscible liquid as a means of removing the water from 95 per cent alcohol to produce absolute alcohol is the Steffens process.[20]

The Glycerin Process. In the process patented by Joseph Van Ruymbeke [21] a different principle is applied. A countercurrent of glycerin is allowed to flow through the still, downward, while the alcohol-water vapor rises. The glycerin acts as dehydrating agent, finally reaching the bottom of the still with all the water combined with it, while the alcohol vapors passing out of the top of the still are low in water, or free from water, depending on the volume of glycerin relative to the volume of 95 per cent alcohol used. The more the relative amount of glycerin, the drier the alcohol. In order to produce 1000 liters of 98 to 99 per cent alcohol, there must be fed in at the top of the still 1000 liters of glycerin.

The glycerin and water passing out at the bottom of the still contain also a considerable amount of alcohol. The alcohol is recovered in second rectifying still, in which the glycerin-alcohol-water solution passes down, while steam, injected at the base of the still, passes upward.

[19] Although absolute alcohol made by this process is essentially pure, it retains enough benzene to give the absorption bands of benzene, in the ultra-violet region.

[20] U. S. Patent 1,670,053.

[21] U. S. Patent 1,459,699.

The alcohol-water vapors passing out at the top of the still are concentrated in other stills in the usual way, while a water solution of glycerin is obtained at the bottom. This dilute glycerin is concentrated as explained in the chapter on Soap and Glycerin, and may then be used over again.

In a later patent,[22] the same inventor adds dehydrating salts such as $ZnCl_2$, $CaCl_2$, K_2CO_3, to the glycerin, and obtains alcohol with 99.8 per cent content. The solution of water, glycerin, salts, and alcohol is distilled with steam, as before, and the hydrous glycerin-salt concentrated *in vacuo* at 160° C.; when desired, the glycerin may be recovered by itself by distillation at reduced pressure.
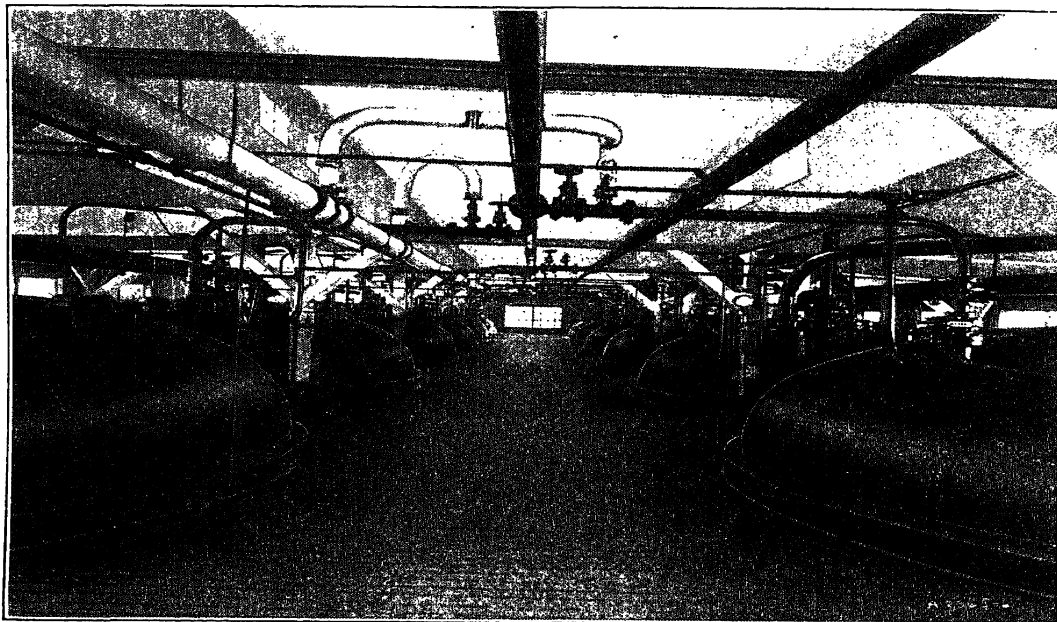
FIGURE 121.—Butyl alcohol fermentation tanks of 50,000 gallon capacity each; only the top of tank is shown at upper level; the tanks extend through the floor to lower level. (Courtesy of the Commercial Solvents Corporation, Terre Haute, Ind.)

ACETONE AND BUTYL ALCOHOL

Acetone and butyl alcohol are obtained by the bacterial action of selected organisms on corn or other carbohydrate. (*See* Figs. 121, 122.) In the Fernbach-Strange process,[23] the organism is designated as "of the type of the butylic bacillus of Fitz," and is allowed to act at 30° to 35° C. in the absence of air; 50 per cent of the malted starch is changed,

[22] U. S. Patent 1,474,216.
[23] U. S. Patent 1,044,368 (1912).

to give acetone and butyl alcohol in the proportions of 1 part acetone to 2 parts of butyl alcohol.   In the Delbrueck-Meisenberg process,[24] the *Bacillus macerans* is spread on fruit peel, asbestos, or other inert material with large surface; the solution containing the sugar with the necessary nutritive material, the same as for yeast, is added; after 5 days the action is complete; 90 per cent of the sugar (best as molasses) is changed to acetone and butyl alcohol.   In the Weizmann process,[25] corn is very suitable; the organism is *Bacillus clostridium acetobutylicum,* cultivated from organisms originally found on the surface of the corn and other cereals.
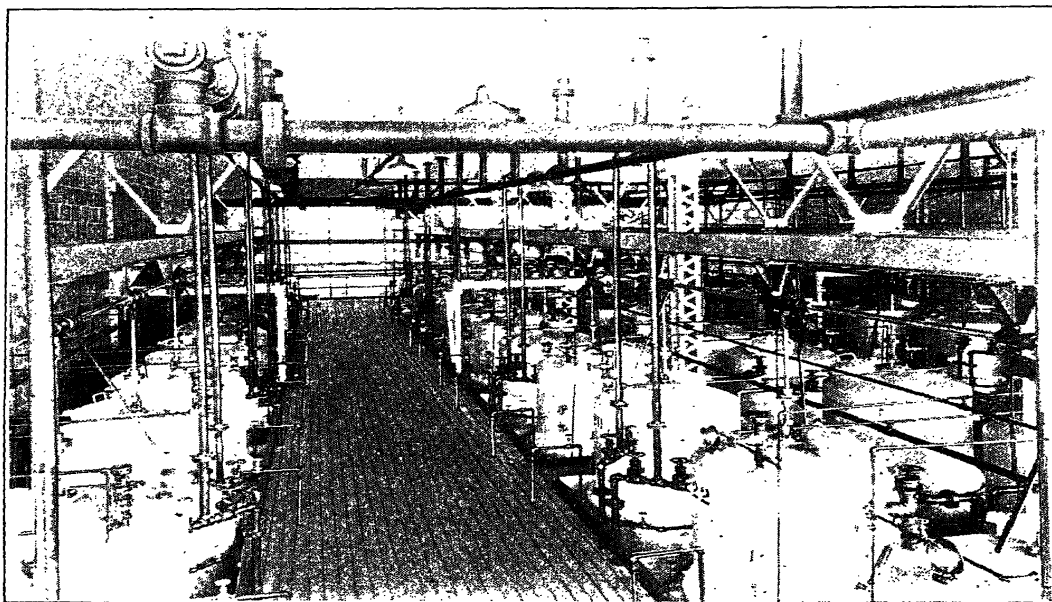
FIGURE 122.—800-gallon bacteria-propagation tanks for butyl alcohol fermentation; one tank furnishes the right amount of culture for one 50,000-gallon fermentation tank.   (Courtesy of the Commercial Solvents Corporation, Terre Haute, Ind.)

The process is as follows: The crude starch from the corn (Chapter 23) is mixed with water in the "mash tuns," then run to the "cookers," closed vessels in which the suspension is heated, giving a thick, sterilized starch paste.   After cooling to 98° F. in water-jacketed coils, the starch paste enters the fermenting tanks; a charge of bacteria culture is added, to 40,000 gallons of paste, 800 gallons of culture.   The action begins after four hours; the jelly-like starch paste begins to liquefy, gradually becoming a thin watery liquid.   At the same time, gases are evolved and pass out with great violence.   Gradually the foaming subsides, and forty-

[24] U. S. Patent 1,169,321 (1916).
[25] Brit. Patent 4,845 (1915).

eight hours after the addition of bacteria to the paste, the action is over. The starch has been converted into liquid products, and gases, hydrogen and carbon dioxide. The liquid products are formed in the ratio of 6 parts butyl alcohol C_4H_9OH, 3 parts acetone, and 1 part ethyl alcohol.

Extreme care is used to protect the *Clostridium acetobutylicum* from outside influences which might decrease its activity. A supply of the pure organism is always at hand, and more put away, mixed with dry, sterilized earth, in which condition it lies dormant for months and even years. A little of the earth is placed with an ounce of starch paste in a test-tube, kept at 98° F.; after one day, it is liquid, and the ounce is placed in a quart of the paste. In one day, this is liquid, and is placed in a 10-quart flask; at one day's interval, transfer is made successively to an 80-quart lot in an enamel tank, then to the final 800-quart batch. Each fermenting vat receives a culture made directly from the dry earth bacteria, over a period of five days.[26]

The purification consists of the following steps: The product of bacterial action, called the "beer," is distilled in order to separate all the volatile substances from the non-fermented residue. The distillate is next separated by a second distillation into the acetone fraction (boiling point 56° C., 132.8° F.), the ethyl alcohol fraction and the butyl alcohol fraction. All three are refined further; the refining of the latter is done in accordance with an interesting patent.[27]

The hydrous butyl alcohol is distilled in a column still with plates, heated by a steam coil; as received from the previous distillation, it contains water. There passes over the constant boiling point mixture containing 70 per cent butyl alcohol and 30 per cent water, at 90° C. (194° F.); on cooling this distillate, it separates into 2 layers, an upper layer with 20 per cent water and 80 per cent butyl alcohol, and a lower layer with 96 per cent water and 4 per cent butyl alcohol. The lower layer is drawn off and sent through the beer stills again; the upper layer is returned to the still, where it forms once more the 30 per cent constant boiling mixture, which passes out. The vapors passing out carry more water than the liquid returned, so that the still gains in butyl alcohol, and loses in water. Some excess alcohol vapor passes out with the constant boiling mixture, but is returned to the still by a dephlegmator kept at 95° C. (203° F.), which condenses it (boiling point 117° C., 242.6° F.), while it allows the 70 per cent mixture to pass out to the cold condenser. Finally the still contains only anhydrous butyl alcohol; this condenses on the upper three plates, free from any impurity, and may be drawn off from there.

Butyl alcohol itself is a solvent in lacquers; besides, it serves to make butyl acetate, a still more valuable and important solvent (*see* table of manufactures), and a number of other esters. Butyl alcohol is manufactured not only by fermentation, but also by synthetic processes.

In 1935, 58,145,494 pounds of butyl alcohol, by fermentation and by synthesis, were produced (9 cents a pound).

[26] From a description kindly furnished by the Commercial Solvents Corp., Terre Haute, Ind.
[27] U. S. Patent 1,394,232 (1921).

The hydrogen and carbon dioxide gases from the fermentation tanks are utilized in the catalytic synthesis of methanol, one of the most brilliant achievements in chemical technology (Chapter 25).

During the war, acetone was greatly needed, ethyl alcohol also, while the demand for butyl alcohol was limited. Efforts were made to develop an organism which would produce acetone and ethyl alcohol only; one such investigation resulted in the culture of a new organism, which was called *Bacillus acetoethylicum*.[28]

Synthetic amyl alcohol, to which reference has already been made in this chapter, is obtained by chlorinating pentane, a low-boiling fraction (28° to 37° C. or 84° to 96° F.) of casing-head gasoline.[29] The chloropentane is then hydrolyzed, giving normal amyl alcohol; amyl alcohol from fusel oil is a mixture of iso-amyl alcohol and optically active (dextro) amyl alcohol.

Lactic Acid. Lactic acid is formed by the action of *Bacterium lactis acidi* on molasses or other sugar-containing material. After dilution, chalk is added, and a nutritive solution, and the action allowed to take place at 40° to 45° C. (104° to 113° F.); the chalk is acted on by the lactic acid as fast as formed, and carbon dioxide given off;

$$2CH_3CHOHCOOH + CaCO_3 = (CH_3CHOHCOO)_2Ca + CO_2 + H_2O.$$

The chalk must be added because the bacteria become inactive if the concentration of the acid is allowed to rise above 1 per cent. The calcium lactate precipitates and is filtered, washed, and treated with dilute sulfuric acid which liberates the lactic acid in solution form. The calcium sulfate is filtered off, the solution of lactic acid clarified, and concentrated to 50 per cent lactic acid, a thick solution. Pure racemic lactic acid melts at 18° C. The 50 per cent solution is used in textile plants, and, especially purified, in certain foods.

The souring of milk is due to the same organism, which forms lactic acid from the sugar in the milk, the lactose.

Citric Acid. Citric acid is made from cane sugar by the action of *Bacillus nigrus citrianus*. The culture is added to a 10 to 12 per cent sugar solution, containing also a suitable nutrient solution, in flat aluminum open pans, at about 40° C. (104° F.). Precautions are taken to keep the various batches from contamination from foreign bacteria. The raw liquor is worked up by adding milk of lime; the citric acid later is regenerated by means of sulfuric acid. The acid liquor is purified by adding sodium ferrocyanide solution, to precipitate any copper and iron, and then concentrated in lead-lined steel evaporators. The strong liquor is crystallized, at rest, to form large transparent crystals, or with agitation, to form granular citric acid, in either case, $C_3H_4(OH)(COOH)_3 . H_2O$. The anhydrous form is in even greater demand than the crystals;

[28] *Ind. Eng. Chem.*, **11,** 723 (1919); or U. S. Patent 1,293,172.

[29] "High-boiling solvents from natural gas pentanes," Lee H. Clark, *Ind. Eng. Chem.*, **22,** 439 (1930).

opaque anhydrous citric acid is made directly from a hot solution by crystallizing at 40° to 100° C. under a high vacuum (730 mm.).[30]

Natural citric acid is made from the juice of lemons, in Italy and California.

The manufacture of glycerin by fermentation is included in Chapter 32.

The commercial importance of a number of substances mentioned in this chapter is indicated by the dollar figures in the Table of Manufactures, at the beginning of the book. For citric acid, the 1935 production was 10,493,064 pounds, at 27.4 cents a pound.

VINEGAR

A dilute alcohol solution seeded with *Bacterium aceti*, after the addition of nutritive solution, causes the formation of acetic acid, provided air has access to the vat. The reaction is

$$C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O.$$
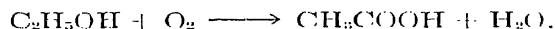
Wines are used to make vinegars, and furnish the strongest (8 per cent acetic acid) as well as those with the best flavor. Cider which has been fermented is largely used, and furnishes a 4 to 5 per cent vinegar.

The *Bacteria aceti* form films which are called mother of vinegar; the souring may take place in casks, the new stock being seeded by leaving a portion of the finished vinegar to mix with it. The more general process is to pour the new stock down shavings which carry the mothers, while a gentle current of air passes upward.

A very fair amount of acetic acid made by bacterial action is used in the chemical industries, as such, and for the manufacture of ethyl and other acetates; generally the dilute acetic acid may be used.

Ethyl alcohol may be changed into acetic acid by catalytic oxidation at elevated temperatures.

OTHER PATENTS

U. S. Patent 1,885,096, process for producing butyl alcohol, acetone, and ethyl alcohol from the same mash; 1,858,808, butyl alcohol and acetone from a mash of waste pulp of a potato flour factory; 1,858,488, propagating yeast in a yeast nutrient solution consisting of a water solution of molasses, urea and in non-ammoniacal inorganic yeast nutrient solutions; 1,766,715, production of lactic acid and its derivatives by fermentation of materials containing carbohydrates; 1,875,536, continuous fermentation process for the production of butyl alcohol; 1,802,163, manufacture of butyl alcohol, by fermenting a mash consisting of molasses, a phosphate, and an addition of malt germs; 1,818,530, continuous manufacture of yeast by the air-fermentation method; 1,380,067 and 1,432,761, chlorine on pentane in presence of activated charcoal and esterification of the amyl chloride at 400° to 450° F. and 250 lbs. pressure; 1,982,160, manufacture of acetic acid from alcohol.

PROBLEMS

1. A Cuban molasses has a specific gravity of 1.4, and the analysis given in the text. There are received 100,000 gallons at Baltimore, brought by tankers; this amount is fermented for ethyl alcohol. The conversion is 90 per cent, and the

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[30] French Patent 724,684 (1931), group 14, class 1.

recovery of the alcohol in the beer in the form of industrial alcohol, 94 per cent. Expressed in pounds of 100 per cent alcohol, how many pounds are collected? If the industrial alcohol is 95 per cent, how many gallons are obtained, the specific gravity being 0.816?

2. The starch contained in one ton of dry corn, with 73 per cent starch, is separated and cooked into a paste. It is then fermented to butyl alcohol and accompanying products as listed in the text. The liquid products are, let us assume, 50 per cent by weight of the starch taken. How many pounds of each are obtained? The parts of the several products are parts by weight.

3. Citric acid anhydrous is made from cane sugar. Over a period of several days, 10 tons of cane sugar are fermented into opaque anhydrous citric acid. The conversion is 75 per cent. The yield in crystal from acid in the hot liquor is 80 per cent. Find the weight of product.

4. A brewery plans to produce 100 barrels of beer a day. How many fermentation tanks will be required, how many mash tons and copper boilers? In order to have the proper capacity, what will be the size and number of the various vessels? Let the fermenting vats be square in cross-section, the other vessels circular. It may be assumed that 105 barrels of wort will be required for the intended production.

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In a democracy, it is necessary to disseminate news readily and cheaply; one of the indispensable agencies in that process is an abundant supply of paper. For the transfer of knowledge from generation to generation, hence for the preservation of knowledge, paper is required. This material is therefore not only a convenience, but one of the cornerstones of our civilization.

Chapter 21

Cellulose from Wood—Pulp and Paper

Cellulose fibers are the basis of any kind of paper. They were formerly prepared from linen and cotton rags exclusively; nowadays such rags are still used to a considerable extent, but the main source of cellulose fibers is wood. There would not be enough rags in the world to manufacture the many tons of paper which are consumed daily by our printing presses, and the cost of collection would make the price too high. Trees may be cut down in the forest, sawed into short logs and floated to the paper mill at a very slight cost; the supply is extensive.[1]

Cellulose fibers from wood are used mainly in two forms: (1) as ground wood, which is merely finely divided wood without purification; (2) in the form of chemical pulp, of which there are two kinds: (*a*) the soda pulp, made from chipped wood by freeing it from the non-cellulose portion by boiling with a solution of caustic soda; (*b*) sulfite pulp, made from chipped wood, by removing the non-cellulose portion by boiling it with a solution of calcium bisulfite. In addition to these pulps which are freed completely from the non-cellulose portion, and are practically pure cellulose, there are products of partially purified cellulose which are used for special products; for example Kraft paper, made by the sulfate of soda process.

The word pulp is used for any one of these products from wood or even rags, so that it is necessary to specify which pulp is meant; there is produced ground wood pulp, and chemical pulp, which latter may be further designated as soda pulp or sulfite pulp. Moreover, the dried fibers made into a wet sheet, as is done for ground wood pulp, or in dry sheets, as is done for the chemical pulps, are termed pulps as well as the suspension made from any one of them with water. In this chapter, the term pulp will be applied to the dry or partly dried material; when made up with water, to a suspension, it will be termed a cream.

Other sources of cellulose are jute, esparto, bagasse, rice hulls, and straw. The process for separating the cellulose from the non-cellulose portions is not unlike the process employed for wood cellulose. Bamboo is also suitable, but it is best cooked with magnesium bisulfite solution.

Making pulp is an industry distinct from that of making paper; pulps of all kinds are products on the open market, sold on demand. Their uses are very numerous; cellulose pulp is consumed (1) for making paper

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[1] But not inexhaustible; one of the major problems of the conservation of our natural resources is that of reforestation due in part to the ruthless cutting down of forests for paper pulps.

of all kinds, paper board, parchment paper; (2) for nitration (Chapters 31, 33, 35, 37); (3) for viscose and other artificial silks; (4) for cellophane; (5) for feminine hygiene articles, surgical dressings; (6) for fillers in plastics; and for other purposes.

The making of paper and the making of pulp are not only distinct industries but different arts, with the former the finer one; this is one reason why they are distinct industries. A second reason is that pulp plants are usually situated in the forest lands near the raw material; the paper plants are situated near the market, that is, near the centers of population. It is cheaper to haul pulp than logs, particularly chemical pulp. In some cases the same company operates a pulp plant as well as a paper-making plant, on the same premises. This is advantageous if the pulp plant is on a river, and not too far from the forest, so that the logs may be floated to the pulp mill, and if there is available at the same time water power to run the paper mill machinery.[2] The haul of the finished paper to the market does not matter so much, since it offsets the haul of the pulp to the paper mill. There also are paper-making plants which bring their logs by railway to the plant, sometimes because power may be had at the plant location unusually cheap, other times because the plant was originally situated in the midst of forest land, which unscientific cutting caused to recede, necessitating the rail haul. In such cases the plant is usually fully paid for by the operations of previous years, so that the resulting lower operating cost offsets the rail haul charge.

The raw material for the pulp manufacturer then is wood or other cellulose-containing materials, and his product is pulp; the raw material for the paper maker is pulp, and his product is paper, either the cheap paper for newspaper, called newsprint, or the somewhat dearer paper for books. The paper maker has an important second raw material in old papers, waste papers, collected from households, printing shops, and business offices in general. Without selection, this waste paper is used to make paper boxes; for making of book paper, it must be sorted, and the cheap grades containing ground wood pulp must be rejected. In the selection, advantage is taken of the fact that a solution of aniline sulfate gives a strong yellow color with paper containing ground wood pulp, and no color at all with chemical pulp papers. The selected chemical pulp paper is freed from ink by a short treatment with caustic soda solution in soda digesters, followed by washing in compartment tanks.

GROUND WOOD PULP

Logs two feet long by four to six inches in width are pressed against a rotating grindstone forming the central part of the grinding device; a number of logs are applied at one time to the grindstone and held against its face by springs. The logs lie with their sides against the stone, so that the fibers are essentially undamaged; if the end of the log

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[2] Such a case is that of the Oxford Paper Company, at Rumford Falls, Maine, from which plant many of the figures used in this chapter are taken.

is pressed against the stone, a useless sawdust results.   Water is fed to the stone, washing away the meal formed, to a storage tank below; if little water is used, hot ground pulp results, which will make a stronger paper; if much water is used, cold ground pulp results, which will produce a weaker paper.   The quality of the pulp is further controlled by the roughening given the stone surface, and by the pressure applied to the logs.

The cream formed is passed over screens (see Fig. 123) or through centrifugal machines, in order to remove coarse particles.   The fibers may be concentrated to a sheet in the wet press machine, consisting essentially of a lower screen-covered, hollow cylinder, three-fourths submerged in the cream, against which an endless felt is pressed.   The water passes through the openings of the screen and flows out to a box placed at the side of the tank; the fibers lie on the screen and are carried by the rotat-
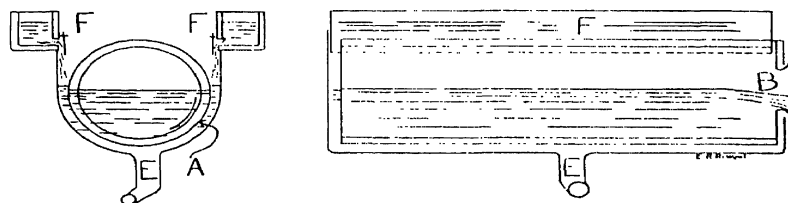
FIGURE 123.—Bird rotary shaking screen. A, slotted screen, which rotates; B, open discharge for cleaned stock; E, waste pipe for tailings removal; F, flow boxes. Driving and shaking mechanism not shown.

ing drum to the felt.   The felt in turn carries it to two finishing rolls, the upper one of which is of wood; the sheet is allowed to coat this roll until a thick sheet is formed, which is rapidly removed at intervals.   The thick sheet is placed in a hydraulic press to remove more of the adhering water; when only 50 per cent remains, it is ready to ship as wet ground pulp, also called mechanical pulp.

This product is now largely made in Canada; it is shipped to the paper-making plant.   Not infrequently, it is made into newsprint at the same plant, and this then shipped to the printers; when this is done, the cream need not be concentrated; it is sent at once to the beater.

MAKING NEWSPRINT

Newsprint contains some chemical pulp; ground pulp alone would give a paper with no strength at all.   For each batch, 1000 pounds of ground pulp and 150 pounds of sulfite pulp are taken and mixed in the beater, together with rosin size and clay; the mixing lasts an hour.   The beater is a refining as well as a mixing device; in the oval containing tank with central partition the cream circulates, actuated by a drum carrying knives parallel to the drum axis.   (See Fig. 124.)   Any cluster of fibers present is disintegrated between the knives and a bed plate against which they work.   The composition of the mix becomes uniform. After one hour the fibers are well disintegrated, and the rosin size is uni-

formly incorporated in the fibers; aluminum sulfate is then added to the cream in order to precipitate the rosin on the fibers. The rosin size is made by dissolving rosin in soda ash solution; it is absorbed by the fiber, and fixed in an insoluble form by the addition of the aluminum sulfate, commonly called alum. A part of the clay is left floating, in suspension; it is retained by the fibers at a later stage, on the screen of the paper-making machine. A further statement regarding the functions of the beaters is given under book paper.

The cream is now ready for the making of the sheet. It is accumulated in two "chests" for each paper-making machine. From the chest it is pumped to a small regulating tank on top of the machine, diluted with a large amount of water drained from previous portions at the wire screen,

FIGURE 124.—The beater; the upper drawing is a vertical cross-section through the wheel side; the lower drawing a top view.
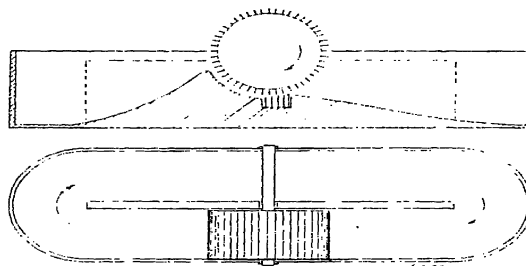
and fed from a final small tank over a weir in the form of a continuous sheet to the rapidly moving "wire" below. The sheet of thinned cream is of the same width as the "wire"; it resembles a waterfall.

The "wire" is the first part of a Fourdrinier paper-making machine which has several modifications adapting it for the making of newsprint. Its details are described further on; the main difference between the use of this machine for newsprint instead of for book paper is that it runs at a higher speed, as high as 900 lineal feet per minute.[3]

Newsprint has the following composition:

Ground wood pulp	1000 lbs.	about 79% on dry basis
Sulfite pulp	150 lbs.	about 12% on dry basis
Loading materials	115 lbs.	about 9% on dry basis

The percentages are given on dry basis, because paper contains a varying amount of water, averaging 5 per cent, even when it appears dry.

THE MANUFACTURE OF BOOK PAPER

In order to show the sequence in the several operations involved in the making of book paper, a simple flow sheet is given below.

Logs → Chippers → Digester → Blow pit → Wash tank ↘

Fourdrinier machine ← Conical refiner ← Beater ← Wash tank   Bleach tank

[3] "Modern pulp and paper making," G. S. Witham, Sr., New York, Chemical Catalog Co., Inc., 1920, p. 50.

Soda Pulp. The ground wood pulp just described is the cheapest of the several pulps; it receives no chemical treatment, no bleaching, and is not refined in special devices. Soda pulp is somewhat dearer; it is a chemical pulp, made from poplar wood chiefly. The logs are freed from bark, and chipped into slices about one-half inch thick. One form of chipper has four knives carried on a large disk, in such a way that only the edge of the blade projects beyond the disk surface; the disk revolves rapidly, and each knife cuts a thin strip from the logs fed along their long axis at an angle to the disk. (*See* Fig. 125.) The slices are fed to a squirrel-cage disintegrator,[4] which reduces them to chips about one-half inch thick by one-fourth inch long. The chips are screened to remove the dust formed, then loaded into a digester, covered with a 10 per cent caustic soda solution, and heated under a pressure of 100 pounds for six hours.

The digesters for soda pulp are cylindrical steel[5] vessels tapering at both ends, unlined, and standing upright. For a digester 6 feet in diameter and 32 feet high, the charge is 11 cords[6] of poplar chips; the product
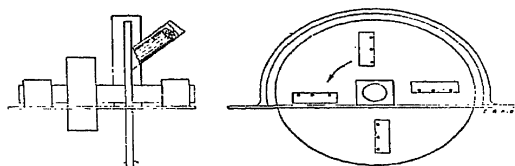
FIGURE 125.—Wood chipper.

is 1200 pounds of pulp, dry basis, for each cord, or $6\frac{1}{2}$ tons per digester. The steam enters from the top of the vessel, and passes through an internal pipe to near the bottom, directly into the liquid.[7]

The discharge is through a pipe at the bottom. A cock is opened when the cooking period is over, and the digester allowed to blow or discharge under its own pressure into a blow pit. While traveling at a high velocity, the lumps of cellulose fibers strike a bronze target and are reduced to small clusters. At the Oxford Paper Company's plant at Rumford Falls, Maine, 27 digesters for soda pulp are blown per day.

The blow pit has a false bottom, permitting the draining of soda liquor, now dark brown because charged with the ligneous portions of the wood. The pulp appears gray; it does not become white until bleached. It is washed free from soda on the countercurrent principle, either in the blow pit itself, or in special wash tanks. Hot dilute liquors are run onto the pulp, of such strength that the liquors will gain in soda content, the pulp lose. The successive liquors are each weaker than the preceding one. Finally water is used, run off, and another portion of water added to make the pulp into a suspension, which is sent to the beater engine if

[4] Chapter 44.

[5] The steel is three-quarters of an inch thick, triple-riveted; welded digesters are coming into favor.

[6] A cord contains 128 cubic feet; it is a pile 8 feet long, 4 feet wide and 4 feet thick and weighs from 2500 to 3300 pounds.

[7] Jacketed digesters are also used; the heating is then indirect.

it is to be used at the same plant. If it is to be shipped, it is made into sheets.

Recovery of the Soda. The soda is recovered as an economic measure mainly, but partly because the disposal of so much alkaline liquor might be prohibited by municipalities or states. The wash liquors are saved, concentrated, evaporated to dryness, and the ash leached for the soda content; it becomes carbonated in the process, and must be causticized with lime before it is used again.

This recovery of soda is less expensive than might be thought, because the brown liquor contains organic matter which on burning furnishes a part of the heat needed. The liquor from the blow pit or wash tanks is concentrated to 40° Bé. in a multiple-effect evaporator; at this strength, it is run into the stack end of a rotary furnace, swept by the
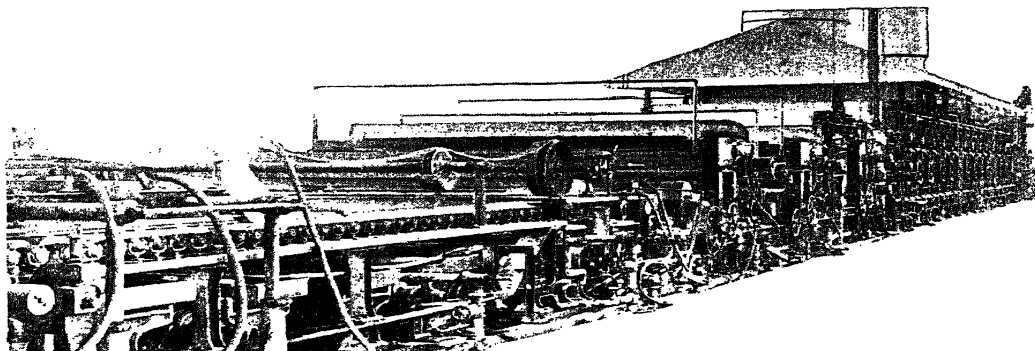
FIGURE 126.—Photograph of a paper-making machine, used for making book paper.

flames from a stationary coal fire. The liquor burns, or more correctly, the organic matter in the liquor burns, carrying off the water and leaving an ash which is black, hence the name "black ash." The black ash contains the soda; it is discharged from the furnace continuously through an opening just in front of the fire, and is leached by water, again on the countercurrent principle. The solution is brought to the proper strength by the addition of fresh soda ash, and then causticized.

If there were no loss, the same amount of soda could be made to digest an infinite quantity of chips; losses occur, however, due to imperfect washing of the pulp and incomplete leaching of the ash; and it is at this stage that the loss is made up. The recovery is 85 per cent, sometimes better. To try to recover the last 10 per cent would be more expensive than the purchase of new soda ash. The causticizing is done by means of lime (Chapter 5).

Sulfite Pulp. Spruce is the wood used chiefly for sulfite pulp. The cellulose fibers are freed from the non-cellulose portion of the wood by digesting the chipped wood with a calcium bisulfite solution containing an excess of sulfur dioxide. A typical sulfite liquor contains 1 per cent

sulfur dioxide combined with lime and 5 per cent free sulfur dioxide. The solution is made in two towers, 70 feet high, of reinforced concrete, lined with acid-resisting tile; the internal diameter is 6 feet. The towers are filled with limestone. Water is fed in at the top of the second tower (second with respect to the gas); weak liquor is collected at the base and fed to the top of the first tower. It passes down the first tower, while the strong gas from the burners enters at the base; there is collected at the base the strong acid ready for the digesters. The gas from the top of the first tower is fed to the second tower, where all of the remaining sulfur gas is dissolved; some air, the nitrogen, and carbon dioxide pass out. Gas as high as possible in sulfur dioxide is prepared, by burning sulfur in flat iron pans air-cooled from below, or in patent burners (Chapter 1). The average strength is 15 per cent. The gas is cooled, and forced by a lead fan into the towers. The reactions are:

$$2SO_2 + 2H_2O = 2H_2SO_3;$$
$$2H_2SO_3 + CaCO_3 + xSO_2 = CaH_2(SO_3)_2 + xSO_2 + CO_2 + H_2O.$$
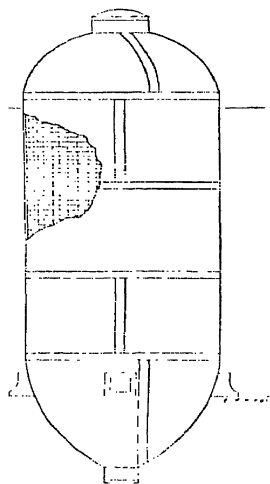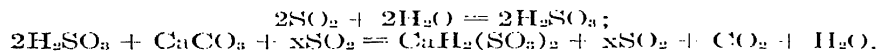
FIGURE 127.—Digester for sulfite pulp.

Another system changes milk of lime to a clear solution of bisulfite of calcium by treating it with sulfur dioxide gas, in tanks run in series, on the countercurrent principle. Instead of burning sulfur, liquefied sulfur dioxide shipped to the paper plant in car tanks is substituted; there are advantages to having the 100 per cent gas at disposal.

The wood is chipped as for the soda pulp, fed to the digesters, the sulfite liquor run in, and the cooking process started. The digesters are steel vessels similar to the digester for soda pulp, but larger; a digester 15 feet in diameter and 50 feet high receives a charge of 28 cords of chipped spruce; the yield is 1062 pounds of pulp per cord, or 15 tons per digester. The cooking period varies with the quality desired; an average one lasts $10\frac{1}{2}$ hours; the blow-off is from the bottom, and the blowpit

similar to the one for soda pulp. The pulp is washed, screened, and either made into sheets for shipment or sent to the beater engines.

The sulfite digesters (*see* Fig. 127) differ from the soda digesters in two particulars: they are lined with hard bricks set in a cement made from litharge, sand, and glycerin; and they develop gas, which must be relieved at certain intervals. The gas is sulfur dioxide, 100 per cent, and is liberated from the calcium compound through the formation of organic salts with the ligneous matter in the wood. The gas is led to towers where it strengthens the sulfite acid from the limestone towers, which is thus made richer, and at the same time provides a way to save the gas. It is this strengthened liquor which has 6 per cent total sulfur dioxide. The cooking is done under a pressure of 100 pounds; the pressure is not allowed to reach above that.

Lime offers among other advantages this one, that any sulfuric acid which might be present is removed in the form of the nearly insoluble calcium sulfate. This is important, for sulfuric acid weakens the fiber. The small amount of sulfuric acid which is formed in the burners and coolers is thus rendered harmless.

The steam is led directly into the liquor, as in the soda process.

Another process for making pulp is the Mitscherlich process, in which the steam is applied indirectly, by means of coils, or jackets.

Bleaching the Chemical Pulps. The gray products from the digesters, whether soda or sulfite, is bleached by means of calcium hypochlorite, $Ca(OCl)_2$. This was at one time bought as bleaching powder; now it is prepared at the mill itself. Liquid chlorine shipped in steel car tanks or in cylinders may be run directly into milk of lime, or it may be gasified first and the gas then passed into milk of lime, using tanks or towers. Instead of purchasing chlorine, many paper mills decompose salt themselves in electrolytic cells, for both products, chlorine and caustic, are indispensable chemicals in the chemical pulp plant. In such cases, sodium hypochlorite is made, instead of the calcium compound.

The pulp from the digester in the form of a thick cream is treated with the bleach liquor and circulated for two hours in a concrete tank having several interconnected compartments; the circulation is provided by a rotary pump. The bleached pulp is carefully washed free from chemicals in compartment tanks.

The production of pulps were as follows:

	1935*		1933*	
	Tons	Dollars per ton	Tons	Dollars per ton
Mechanical pulp	1,355,819	18.50	1,197,553	19.70
Sulfite pulp	1,594,748	44.80	1,327,575	41.00
Soda, semi-chemical pulp....	489,238	37.20	457,790	36.25
Sulfate pulp	1,467,749	24.50	1,259,351	23.10

* Bureau of the Census.

The Beater Engines. The white pulp from the bleacher tanks reaches the beaters next, where it is freed from lumps, and where the sizing material, the clay, and later the aluminum sulfate solution are added and the

whole made homogeneous. The beaters are of many forms; the type shown for newsprint (Fig. 124) embodies the essential principles; in size they may be 28 feet long, 12 feet wide, and 4 feet high. For papers in which only chemical pulp enters, such as book papers, the period of beating lasts several hours; the sizing is added at the start, the clay next, then a coloring matter if one is to be used, and near the end of the beating period, the solution of aluminum sulfate.

The beater or Hollander is (a) a mixing bowl, in which the suspended fibers and the several additions are intimately mixed, except for the one added last, the "alum", which precipitates an aluminum soap on the fiber, closing its capillaries which otherwise would absorb water too readily in the finished paper; (b) a beating device, in which the fiber is frayed, and a gelatinous material formed which on drying and pressing cements the fibers together into a strong sheet of paper. "The felting of the fibers into a sheet of paper is brought about by the cohesion of the colloidal aggregates."[8] Clots are separated into their constituent fibers. Finally, (c), in the interest of strength in the finished paper, there should be no cutting of the fibers in the beaters; a certain amount of cutting is unavoidable, but so slight as to be negligible. When desired, the beater may be made to function so as to cut the fibers; to this
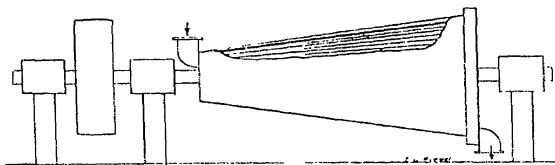
FIGURE 128.—The conical refiner.

end, the wheel filling is brought closer to the bed plate, and the filling (knives) is changed from a broad-faced one to a slender-faced one.

Provision is made for running off the "beaten stuff," which is fed to the conical refiner.

The Conical Refiner. The conical refiner, often called the Jordan,[9] follows the beater engine; its action is to separate and cut the fibers, but it can select the fibers which need cutting, the clusters which still persist, and work on them, letting the properly reduced portion pass through without expenditure of power.

The refiner consists of a stationary outer cone bearing knives projecting inward, and a rotating inner cone bearing knives projecting outward, so that the edges of the two series of knives meet. (*See* Fig. 128.) The knives are held in place by wooden strips which are depressed, forming channels. The suspended pulp enters at the narrow end. It travels in the channels of the rotor; centrifugal force sends the coarse particles into the upper channels, but leaves the fine material unaffected. The coarse

[8] P. 69, "Production and treatment of cellulose in the paper industry," James Strachan, *Trans. Inst. Chem. Eng. (London)*, 7, (1929).

[9] Invented by Joseph Jordan, of Paterson, N. J., 1862.

particles fall back on the knives after they travel a little further, for the casing widens, so that only a greater centrifugal energy would keep the coarse stuff in place. The knives reduce the clusters, which then travel further; if incompletely separated or cut they are again thrown into the channels of the outer casing, and again fall on the knives. In the lower half of the refiner such interplay is not possible, and there no work is done; as a result only the upper part of the casing wears.

From the refiner, the suspension is pumped to a chest at the top of the paper-making machine, diluted with water drained from previous portions to a very thin suspension having the appearance of skimmed milk, and passed through a rotary, shaking screen, and, for very clean stock, through the centrifiner.

The Bird Centrifiner. Besides removal of foreign matter by screens, the stock may be cleaned by centrifugal force, in the Bird centrifiner,[10] which removes both light and heavy impurities. In Figure 129 the passage
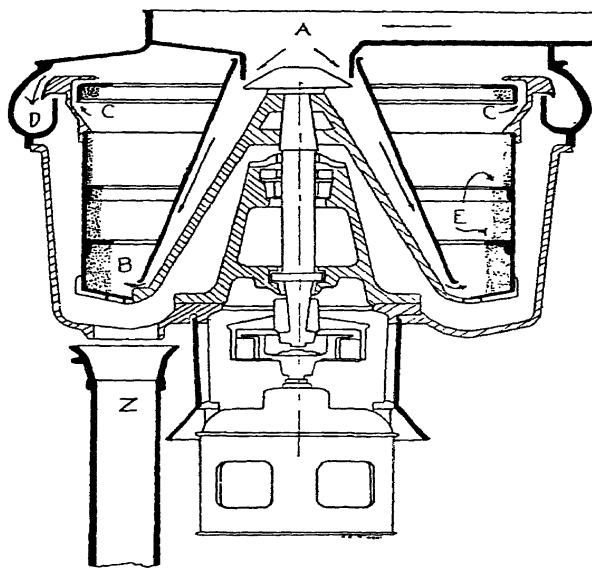
FIGURE 129.—The Bird centrifiner. *A*, raw stock inlet; *B*, matte with dirt retained by annular baffles *E*; light dirt caught by annular skimmer *C*; *D*, cleaned stock, with outlet to paper making machine; *Z*, waste pipe for washings.

of the stock through the centrifiner is indicated. The stock is forced against the wall of the rotating machine, the heavy particles remaining under the baffles *E*, while the dirt lighter than the fibers is held by the skimmer, *C*. The cleaned stock collects in *D* and flows thence to the paper-making machines.

It is recommended that the centrifiner be placed after the conical refiner, and ahead of the final screen at the head of the paper-making machine. Each device fulfills a definite distinct function, and in the proper sequence.

[10] The Bird Machine Co., South Walpole, Massachusetts.

The centrifiner is still a new device. It is designed for use in all grades of paper; in the size made at present (for 7000 gallons per hour), it is particularly adapted to smaller machines making high-grade rag paper and tissue machines.

The Fourdrinier Engine. The original paper-making machine developed by the London firm of stationers, Messrs. Fourdrinier, assisted by Mr. Bryan Donkin, in 1803, has been modified only slightly in principle, although very much in size and complexity. The original inventor, the Frenchman Louis Robert (1798), used an endless perforated metal screen to make a continuous sheet of paper instead of the separate smaller pieces laboriously made by the older hand process. This fundamental idea was the one the Fourdrinier firm developed.

In the modern machine it is well to distinguish between the wet end, where the "wire" is located, and the dry end, where the dried sheet of paper is collected. Beginning at the wet end, the machine consists essentially of an endless woven wire which receives the thinned suspension of pulp, couch rolls which press out the water, felting which
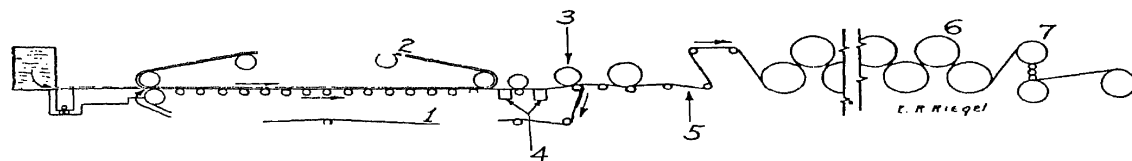
FIGURE 130.—A simplified Fourdrinier machine showing the principal parts: 1, the wire screen; 2, deckle straps; 3, couch roll; 4, suction boxes; 5, wet sheet of paper; endless felt which supports the paper not shown; 6, drying cylinders; 7, calender.

carries the wet sheet while it is weak, drying cylinders which remove the remaining moisture, and a calendering machine which gives by pressing a smooth surface to the paper. A simplified machine having only the essentials is shown in Figure 130.

The Endless Wire. The woven wire receives the thin suspension of pulp at one end, carries it forward while water is drained off, and delivers at the far end a sheet of wet paper. A jerky sidewise motion is given the "wire" in order to cause the fibers to become meshed into each other. They lie mainly in one direction, that of the travel of the sheet; without the sidewise vibration, paper would have no strength at all in the lengthwise direction; the weaving gives it a moderate resistance. The strength of the paper in the direction crosswise to the line of travel is considerable, because the tear must pass through the fibers lying across its path.

The rate of travel of the endless "wire" determines the rate at which the paper sheet is made; a high speed for book paper is 365 feet per minute; that is, every point on the sheet travels forward at that rate. The speed varies according to the weight of the paper. The width of the "wire" varies also; a wide one for book paper would be 164 inches

for the wire, giving a finished sheet 148 inches wide. The wire screen is woven bronze, with perhaps 40 cross wires to the inch and 80 lengthwise wires to the inch. It runs on numerous small rolls, which carry off much water; suction boxes are placed under the screen at the farther end, to remove still further quantities of water. Wire and cloth both pass through two rolls, the couch rolls, which press out so much more of the remaining water that the sheet is now merely wet paper. An endless felt is run under the sheet at the exit from the couch rolls and such felts, made up in various sections, carry the paper over the drying cylinders. With a 60-foot wire,[11] the suspended fibers are made into a wet sheet of paper in 10 seconds.

The suspension is prevented from running off the screen by the deckle, which consists of an endless rubber belt for each side; the belts run at the same speed as the screen, so that at all times two edges are provided in which the suspension is caught.

The Drying Cylinders. The wet sheet of paper supported by the felting passes over a great number of warm and hot cylinders which evaporate the water. The cylinders are usually four feet in diameter, and as wide as the screen; they are heated by steam, introduced through the trunnions, since these cylinders rotate. Only one cylinder pulls the sheet, the others are really idlers, rotated, however, by a drive, so that their speed is exactly the same as that of the paper. The cylinders near the dry end revolve somewhat more slowly than the others, because as the paper dries, it shrinks; the same speed as near the wet end would cause it to tear.

The Calender. The dried sheet is passed over six rolls mounted vertically; three rolls are smooth iron, and heated internally by steam; three are covered with felt in order to grip the paper. All travel at the same speed. The weight of the rolls presses the warmed paper and reduces its thicknesses by 40 per cent; the interstices between the fibers are thus decreased; the surface becomes smooth, so that a pen no longer catches in the fibers. Without the process of calendering, the sheet would be blotting paper.

Cylinder Machines. A considerable amount of paper is made on cylinder machines. Two or more cylinders, 36 inches by 42 inches long, turn in the suspension of fibers which has passed the conical refiner and rotary screen; the fibers coat the outside of the wire, while the bulk of the water flows inward and is pumped off fast enough to establish a lower level inside the cylinder. At the top of the cylinder, a felt picks up the layer of fibers, and carries it through squeegee rolls, and further to the driers. Such machines are used for tissue paper, for manila envelopes, and thin boards. For a five-ply board, five cylinders are used, each one dipping in the fiber suspension; the sheet from one cylinder feeds onto the sheet from the second, and so on, the five sheets becoming one.

[11] Total length 120 feet; feet traveling forward, 60 feet returning underneath to the starting point.

BOOK PAPERS, COATED PAPERS, BOARD PRODUCTS, KRAFT PAPER

The two chemical pulps are mixed for book paper, usually one-third sulfite pulp (spruce) to two-thirds soda pulp (poplar). It is apparent that there must be a difference in the pulps, since the mixing is always done. The fibers in sulfite pulp are longer, tougher, and stronger than those in soda pulp; the latter give fineness of surface and a velvety feel. Envelopes and writing tablets contain rather more sulfite pulp than the proportion given above; the result is a harder paper, but stronger. In price, the difference is small; bleached sulfite pulp is around forty-five dollars a ton, bleached soda pulp thirty-seven dollars, with rather wide fluctuations.

One form of book paper is rough, bulky, and light; it is called featherweight, and is nearly pure wood cellulose. It permits making a book with maximum bulk, with minimum printing expense.

Enameled or coated papers receive a special treatment after the usual calendering. English china clay, blanc fixe (barium sulfate), satin white (aluminate of lime), or Paris white (carbonate of lime) are suspended in a casein solution and applied in a special coating machine; the resulting surface is truly porcelain-like, and well named enamel. Such paper is used for fine half-tone printing and high-grade books.

Paper box products are made from waste paper without sorting it; a small amount of sulfite pulp is added; cylinder machines are used.

Kraft papers are made by the sulfate process, with insufficient digestion, so that much ligneous matter remains; at the same time longer fibers persist, resulting in a paper which is brown in color, but strong, and well adapted for making wrapping paper and bags. In the sulfate process, the chipped wood is digested with a solution of salt cake, or sodium sulfate, which, however, has previously been reduced by means sawdust so that it contains not only sodium sulfate, Na_2SO_4, but also sodium sulfide, Na_2S, sodium hydroxide, $NaOH$, and sodium carbonate, Na_2CO_3. The digestion proceeds in unlined steel vessels as in the soda process, but lasts only $3\frac{1}{2}$ hours. The pulp passes through beater and conical refiner as white paper does, and is made into a sheet on a Fourdrinier.

Paper has been made from straw in the United States for many years, and on the large scale. Since 1903, the inner sheet of corrugated paper, which carries the actual corrugations between the flat top and bottom liners, has consisted of unbleached straw paper; its color is a characteristic green-brown. Pulp from straw is made in Ohio, Michigan, and several other states. The process was originally the soda pulp procedure; it has become more specialized. Of late, wheat-straw bleached pulp has been made the Pomilio system [12] by "gas chlorination." The process consists of (a), a leaching with warm 1 per cent caustic soda; the solids are pressed out of the suspension, the press cake torn to shreds, and (b), chlorinated by means of chlorine gas. Next the material is washed with

water, and is then (c), agitated in Hollander-like vessels with cold dilute caustic, which dissolves the chlorinated non-cellulose portions. After washing again, the pulp is fed (d), to bleaching Hollanders, with the necessary calcium hypochlorite. The bleached pulp is stored until required by the paper mill.

To produce	there are required:**
2000 lbs. air-dry wheat-straw pulp	4200 lbs. wheat straw
	1150 lbs. common salt
	800 kw-hr. for electrolysis
	200 kw-hr. for motors

** *Ind. Eng. Chem., News Ed.,* **13,** 436 (1935).

TABLE 35.—*United States Production of Paper and Paper Board for 1935, in Tons (Bureau of the Census).*

Newsprint	1,221,871	Tissue paper	473,314
Book paper	1,281,870	Absorbent paper	95,179
Writing paper, fine	514,486	Building paper	463,143
Kraft paper for bags	394,576	Boards	4,722,890
Kraft wrapping paper	590,208	Kraft liners	710,323
Other wrapping paper	647,270	Jute liners	801,086
Greaseproof	12,404	Straw liners for corrugated boards	346,415
Glassine	37,346		
Cardboard		103,053	

OTHER PATENTS

U. S. Patent 1,837,309, production of sulfite pulp and recovery of the acid employed; 1,872,996, process of making pulp, subjecting the treated material to a steam pressure of over 250 pounds/sq. in. and discharging at that pressure so that the material is exploded and thoroughly distintegrated; 2,031,974, recovery of chemicals from waste pulping; 2,069,185, manufacture of vanillin from waste sulfite pulp liquor.

PROBLEMS

1. A soda pulp digester has a capacity of 820 cubic feet. It contains at the end of the cook 220 cubic feet of cellulose fibers. In the remaining space, a volume equivalent to 500 cubic feet of cold 5 per cent caustic soda, with specific gravity of 1.05, is introduced. What was the weight of the cold caustic liquor, how much caustic soda in pounds did it contain, and what was the volume of the 5 per cent caustic soda solution in gallons?

2. A sulfite pulp digester has a capacity of 3000 cubic feet; it contains a 6 per cent calcium bisulfite solution to the extent of two-thirds of its volume, measured cold. Let the specific gravity of the solution be 1.07. How much calcium bisulfite is represented, how much sulfur dioxide, and how many pounds of sulfur would be required for the production of one-half this quantity of sulfur dioxide?

3. A wood contains 50 per cent cellulose. It is desired to produce 56 tons of a certain paper per day, from chemical pulp. How many cords of wood will be required, using the values given in the text? The yield of paper on the basis of cellulose in the wood is 90 per cent.

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The main natural filaments used for articles of clothing are three: wool and silk, of animal origin, and cotton, of vegetable origin. To these the chemical industry has added a fourth, called artificial silk or rayon, which rivals in beauty the natural silk. Besides rayon proper, mainly viscose rayon, there is now cellulose acetate, softer, and stronger when wet.

Chapter 22

Cellulose from Wood and Cotton—Artificial Silk

Artificial silk is made chiefly from cellulose from wood and cotton by recasting it in thin threads, which possess the softness and the sheen of real silk. Unlike most other industries which grew out of trials and practices unconnected with scientific reasoning, this new filament is a gift on the part of modern inventive genius following scientific rules and employing chemicals and reactions with the freedom of the chemical expert. This new material has found considerable use in the manufacture of underwear, stockings, fabrics, carpets, scarfs, and similar articles. When wet, rayon loses 70 per cent or so of its strength, while real silk hardly loses at all in strength. By weaving artificial silk with worm silk, a material results which is almost as strong as the one made from worm silk alone, but considerably cheaper and therefore able to command a wider market. The market for worm silk itself has reflected this new use as shown by the figures below:

TABLE 36.—*Raw Worm Silk Importations Into the United States.**

	Pounds		Pounds
1924	46.171.863	1930	82.008.164
1925	59.137,648	1931	89.446.101
1926	64,290.934	1932	74,052.521
1927	73.402,000	1933	67.245,130
1928	88.269.768	1934	56.379.322
1929	98,016,151	1935	67,674,918

* Bureau of Foreign and Domestic Commerce.
Note: No worm silk is raised in the United States.

The artificial silk industry may, therefore, be regarded as supplementing the worm silk production, rather than rivaling it. Weaving artificial silk with wool and with cotton has resulted in new fabrics of great merit and popularity.

The new filament is now called by a name of its own, namely, rayon, in order to emphasize its characteristic nature, a synthetic product which can make its way without pretending to be a form of silk. The name has been adopted in the United States, and to some extent in Europe; it will be used in the present discussion. While rayon proper is cellulose regenerated, cellulose acetate is an ester of cellulose, and should be in a group by itself; it is frequently included in the tabulations for "rayon," nevertheless.

The reason for the increased use of rayon is its comparatively low price. The 150-denier thread, 60 filaments, a standard size much in demand, on March 31st, 1937, was 65 cents a pound. In 1931, raw silk imported averaged $2.29 a pound; it has dropped still further since, ($1.20 in 1933), but has risen again; in early 1937, the quotations lay between $2.05 and $2.27 a pound. Rayon is between one-third and one-fourth the price of worm silk. Acetate silk was considerably higher than viscose, some time ago, but by 1936, its quotations were not greatly different from those for viscose rayon.

TABLE 37.—*Prices (U. S.) for Spun Rayon by Deniers for 1935.**

	Per pound
Finer than 100 deniers	84.8 cents
100–124 deniers	71.3
125–150 deniers	52.3
Heavier than 150 deniers	48.0

* Bureau of the Census.

The size of the thread is designated by the number of deniers.[1] The standard generally used is the Italian denier, which is the weight in grams of 9000 meters of thread. Thus a yarn is said to be 150 deniers,
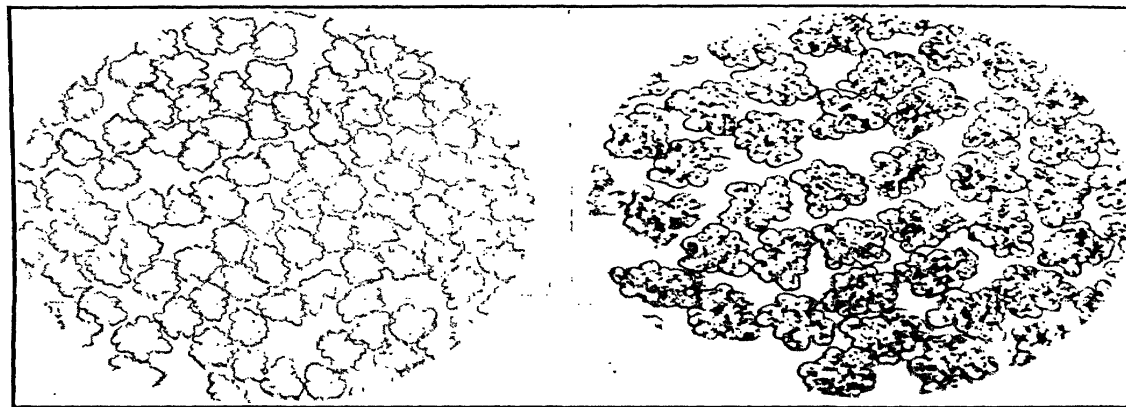
FIGURE 131.—Micrographs of a cross-sectional slice of the rayon thread, showing the several filaments, for a clear viscose [left], and for a delustered one [right]. Courtesy of the Research Laboratory, Technical Division, Rayon Department, E. I. du Pont de Nemours and Company, Buffalo.

if 9000 meters of it weigh 150 grams. The smaller deniers are finer threads; the larger deniers are coarser. Threads as low as 40 deniers are made, and are rather dearer than the medium sizes (150 deniers); while threads as high as 450 deniers are also made, and are rather coarse. In any case, the thread whose denier is under discussion is itself made up of a number of filaments.

[1] The smallest piece of medieval French money was called a denier.

The rayon industry is a brilliant example also of how inventive genius may transform a cheap material into a valuable one. Wood pulp from which rayon is made is worth less than 2½ cents a pound; while after it is spun into threads, it brings 65 cents a pound. It must be added at once that many operations with careful supervision are necessary, and that only a large plant can hope to operate at a profit.

For the year 1935, the U. S. production of all types of artificial silks was 285 million pounds, the world production 1,265 million pounds.

TABLE 38.—*World Production Figures for Rayon Including Staple, for 1936.**

	Millions of pounds
Japan	315
United States	285
Italy	165
Germany	150
Great Britain	150
France	70
All others	130
World total	1,265

* Rayon Organon.

Staple rayon is a newcomer; it consists of short lengths of rayon fiber intermingled as cotton fiber is. The United States production in 1936 was 27 million pounds, and Japan's, 50 million pounds.

METHOD OF MANUFACTURE

The manufacture of artificial silk, by any process, is essentially as follows: A solution of cellulose is prepared, viscous enough to form a liquid thread; such a liquid is forced through a small opening, and the liquid thread formed is made to pass through a chemical bath or a current of air which causes the liquid thread to solidify instantaneously. A suitable mechanical arrangement of pulleys, drums, and bobbins provides for the removal of the solidified, wet thread. The thread must then be washed, perhaps treated in a chemical way, dried, twisted, reeled into skeins, and in general handled as silk would be. There are needed then: a cellulose solution, a device for ejecting the thread, a coagulating or precipitating medium, another device for gathering and winding the thread, and auxiliary appliances.

The various processes are characterized by the nature of the cellulose solution, but they also differ in the chemical treatment of the liquid thread, and in the method of spinning and gathering. The four important processes are the nitrocellulose process, the viscose process, the cellulose acetate process, and the cuprammonium process. Although only cellulose is mentioned as suitable material, other substances have been tried, of which gelatin was perhaps the most promising. Up to the present, no material which might replace cellulose has been introduced into the industrial field.

The nitrocellulose process is the original process for artificial silk,
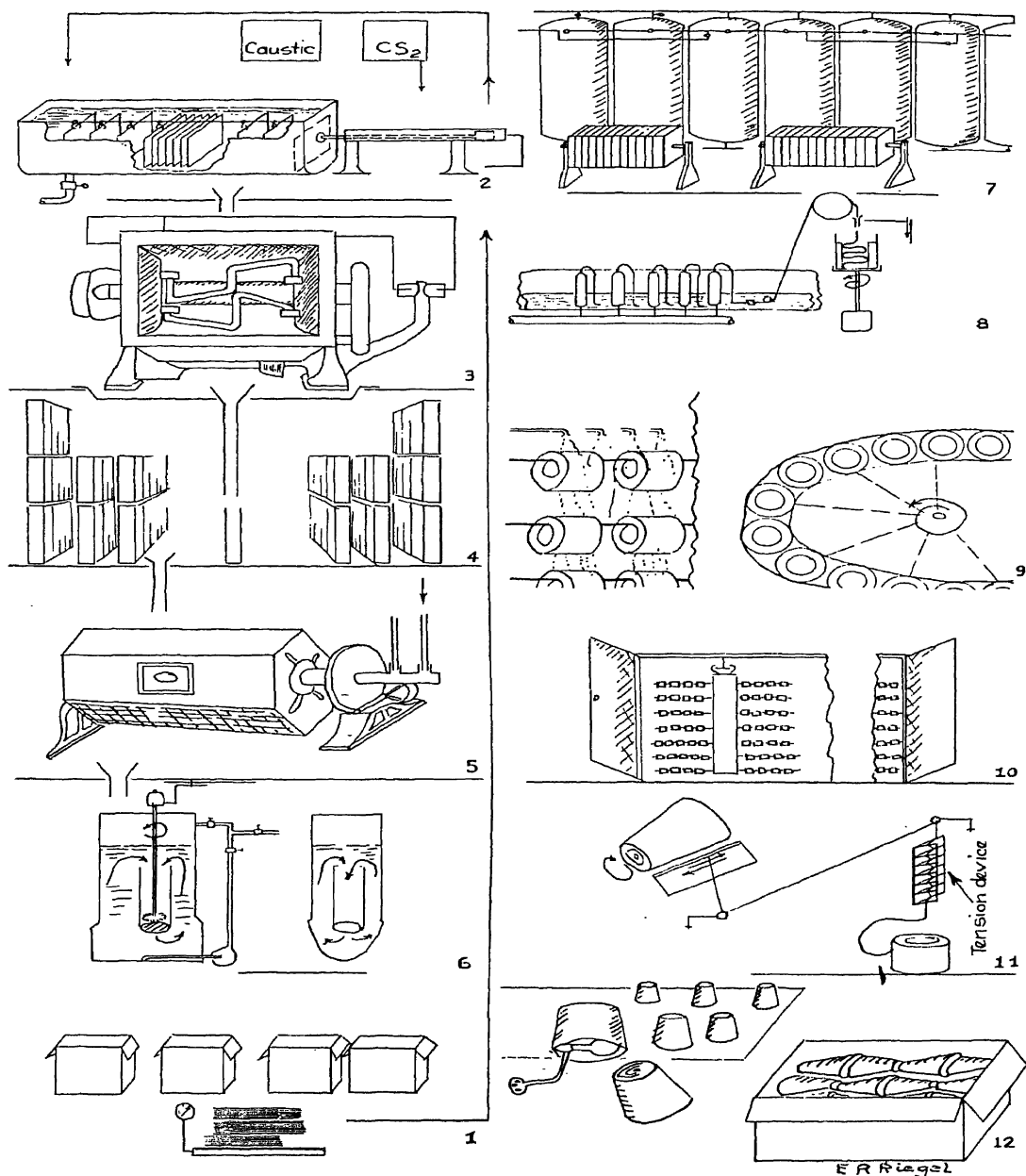
FIGURE 132.—Flow sheet for the viscose rayon process.

1, sulfite pulp sheets storage
2, caustic swelling tank
3, shredder
4, aging of alkali cellulose crumbs
5, xanthating churn
6, mixer for dissolving the xanthate in caustic

7, viscose aging tank
8, spinning machine
9, left, desulfurizing, bleaching, washing of cake; right, centrifuging
10, drying
11, winding into cones through tension device
12, inspection and shipment.

invented and patented by Chardonnet[2]; the first plant was the one at Besançon, France. It is not used in the United States, and probably no longer anywhere else.

THE VISCOSE PROCESS

The viscose process is at the present time the most successful; of the American production, 77 per cent (1936) is viscose rayon, and the proportion for the world production is similar. This process has the great advantage of requiring only inexpensive materials for the production of rayon—sulfite wood pulp,[3] sodium hydroxide, carbon disulfide, acid sodium sulfate, sulfuric acid, and some others in smaller quantities. The product is not flammable. The process is based on the discovery, made in 1892 by two English chemists, Cross and Bevan,[4] that mercerized cellulose or alkali cellulose forms a definite though unstable compound with carbon disulfide. This compound, called cellulose xanthate, is a yellow solid; its formula may be written

$$(\text{Cellulose}) \text{ONa} + \text{CS}_2 \qquad \text{C} \begin{array}{l} \diagup \text{O (Cellulose)} \\ \diagdown \text{SNa} \end{array}$$
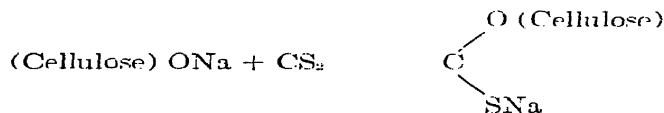
It is soluble in dilute caustic soda, and from this solution cellulose is rapidly precipitated by an acid. The process will at once be clear: alkali cellulose is combined with carbon disulfide, the product dissolved in dilute caustic, producing a viscous solution, called by the discoverers viscose. The solution is sent to the spinning device, and the issuing thread coagulated by a bath of sulfuric acid. This is a list of the essential steps; a few details may now be added.

The sulfite pulp used is carefully selected, and secured always from the same source; it is steeped in a caustic soda solution, and allowed to ripen. It is then shredded to crumbs and in that form is known as alkali cellulose. The crumbs are next agitated with carbon disulfide and the xanthate formed is dissolved in a caustic soda solution, producing the viscose solution. The viscose is stored for a number of hours before spinning.

Alkali Cellulose. A batch of 125 lbs. of sulfite sheets is made up by drawing on all the carloads in the storage room, a few sheets from each, to insure uniformity. It is placed in 18 per cent NaOH for a period of, let us say, 60 minutes, with the temperature regulated (jacket to steeping tanks) to 18° C. (64.4° F.). The α-cellulose (86 per cent of the pulp) does not dissolve; it swells; β-and γ-cellulose are dissolved and carried away by the caustic as it is drained off. The swollen sheets are pressed by a ram, and dropped to the water-jacketed shredder below, where the

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[2] It is pleasant to know that Chardonnet was at one time a student of Pasteur. Chardonnet's basic patent was French Patent 165,349 (1884). [Quoted from Mr. Avram's book "The rayon industry," New York, D. Van Nostrand Co., 1927].

[3] Chapter 21.

[4] The first patent for this process was Brit. Patent 8,700 (1892).

alkali cellulose is reduced to soft crumbs. The crumbs pass to the floor below, to be stored in narrow steel containers for a period of 2 days or so, with the room temperature controled by conditioned air. This constitutes an aging period.

Xanthate. The equivalent of a shredder is charged into a water-jacketed churn to which, after a few minutes of mixing, carbon bisulfide is added; the churn rotates for 2 hours, at the rate of 2 R.P.M. The
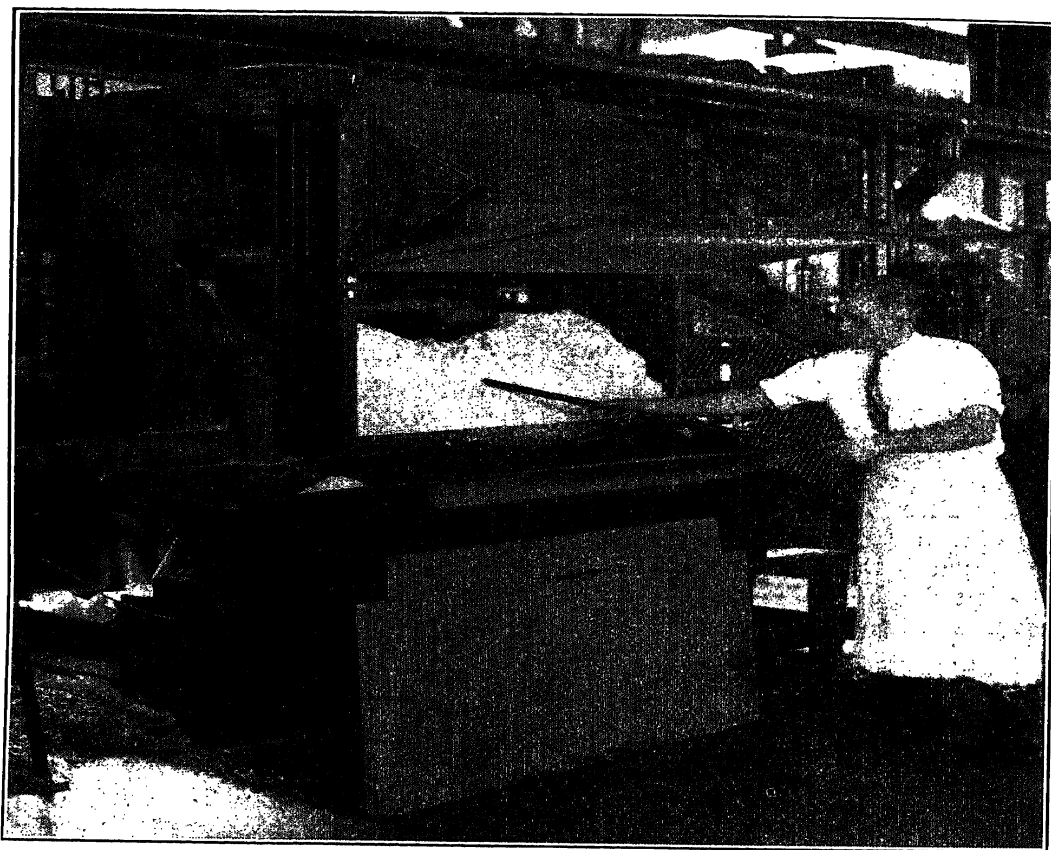
FIGURE 133.—The alkali cellulose shredder in a rayon plant. (Courtesy of E. I. du Pont de Nemours and Company, Rayon Department.)

orange cellulose xanthate is formed; it has the appearance of wet saw-dust. The excess carbon bisulfide vapor is drawn off through a horn, and the xanthate discharged into a mixer below, and sodium hydroxide (caustic soda) solution added, and by means of a stirrer and a circulating pump, the xanthate dissolved (2 to 4 hours). The mixer in turn is discharged into the blender, 4 mixers to the blender, 2 churns to the mixer, 1 shredder to each churn, and two press tanks to the shredder; hence, the blender

represents 2,000 lbs. of original cellulose. The solution now contains 7 per cent cellulose and 6 per cent caustic; it is thick and viscous, hence the name viscose is appropriate. All water used is distilled water. The

FIGURE 134.—The tanks in which the viscose is stored. aged, filtered. and liberated from bubbles by applying a vacuum. (Courtesy of E. I. du Pont and Company, Rayon Department.)

caustic from the steeping presses is sold to a soap maker, if possible; if not, its caustic values are salvaged by osmosis cells, while the dissolved cellulose is discarded.

The Viscose Solution. The viscose is a *clear* viscose and is suitable for lustrous viscose products. For the *dull* or semi-dull viscose, there is added

at this stage a colloidal suspension of titanium dioxide whose particles are 5μ or less in diameter; the viscose so treated is cloudy; when spun the fibers are without lustre. The viscose now passes into the spinning department, entering a system of tanks in which it may be held for aging, 1 or several days; it is filtered from any material exceeding 5μ, and by means of an applied vacuum, the bubbles which it has collected are pulled to the top and destroyed. The temperature while aging is 19° C. (66.2° F.); the longer the viscose ages, and the higher the temperature, the more readily does it flocculate, the lower the salt index. The viscosity-time curve has a sharp break, and the aim is to spin the viscose close to the break, but before it is reached. The process while aging is a hydrolysis of the xanthate, forming hydroxycellulose, which leads to the formation of di, and then tricellulose xanthate, and with the cellulose units hydrated, while a corresponding amount of carbon bisulfide and caustic are liberated.

$$3\underset{\text{original xanthate*}}{\overset{\text{O}.\,C_6H_9O_4}{\underset{\text{SNa}}{\overset{|}{C}=S}}} \quad +2H_2O \longrightarrow \underset{\text{aged xanthate}}{\overset{\text{O}.\,C_{18}H_{27}O_{12}(OH)_2}{\underset{\text{SNa}}{\overset{|}{C}=S}}} \quad +2CS_2+2NaOH$$
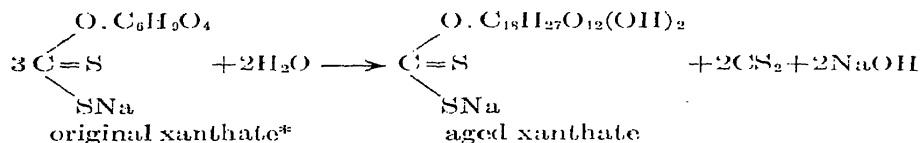
* In the aged cellulose xanthate, the cellulose molecules form a complex. The number of $C_6H_{10}O_5$ groupings in the xanthate is shown as one merely for simplicity; the number is larger, but its exact value has not yet been settled.

Salt Index. To test the ripening of the viscose, one drop is placed into a salt solution, and its coagulation observed. The salt solution is made up by running in 3.2, 4.2, 6 cc., or more, of a strong stock solution into enough water to make the whole 40 cc., in an Erlenmeyer flask, which is then shaken one-half minute. The proper action is the division of the drop into 3 flocks. The less ripe solution requires more salt for the coagulation. The ripening is right when the "salt index" is 3.2 to 4.2. A variation in ripeness means variations in a number of physical properties, such as tensile strength and dye acceptance. For a short time, the properly aged solution may be preserved unchanged in the right state for spinning at 0° C. (32° F.).

The Spinning Machine. There are two types of spinning machines for viscose, the bobbin machine, and the more favored bucket machine. The latter has a rotating bucket, essentially a small centrifugal, in which the thread accumulates; at the same time the bucket speed produces a twist in the slower traveling thread, thus eliminating one complete textile operation, that of twisting. Bucket spinning is also called pot spinning. The bobbin machine, on the other hand, does not twist the thread. As a rule, 50 spinnerets are mounted in a row, on one side of the aisle, and with another bank of 50 on the other side; the row is about 50 feet long. There are a great number of such aisles in the plant. Each spinning unit has a small pump, either piston or gear (preferred), a small filter, the candle filter, the spinneret proper, also called the jet, a coagulating bath, either in one long trough for the row or in separate bowls, and the gather-

ing device consisting of the feed wheel, the guide and the bucket (or, in the case of the bobbin machine, a wheel for winding the newly made thread). The small filter is the size of a candle, and contains a calicot stocking through which the solution must travel; it is surmounted by a curved tube dipping into the coagulating bath and carrying at its extremity the spinneret. The latter is a flat cup the size of a small thimble; it was

FIGURE 135.—A bank of the bucket spinning machine for r a y o n , with the deck removed to show the working parts. Beginning at the left b e l o w, switch for motor, pump, candle filter (at an angle), motor d r i v i n g the bucket, bucket with cover and c o v e r clip, and near the top, feed w h e e l. (Photo, Dr. Paul Wolff.)
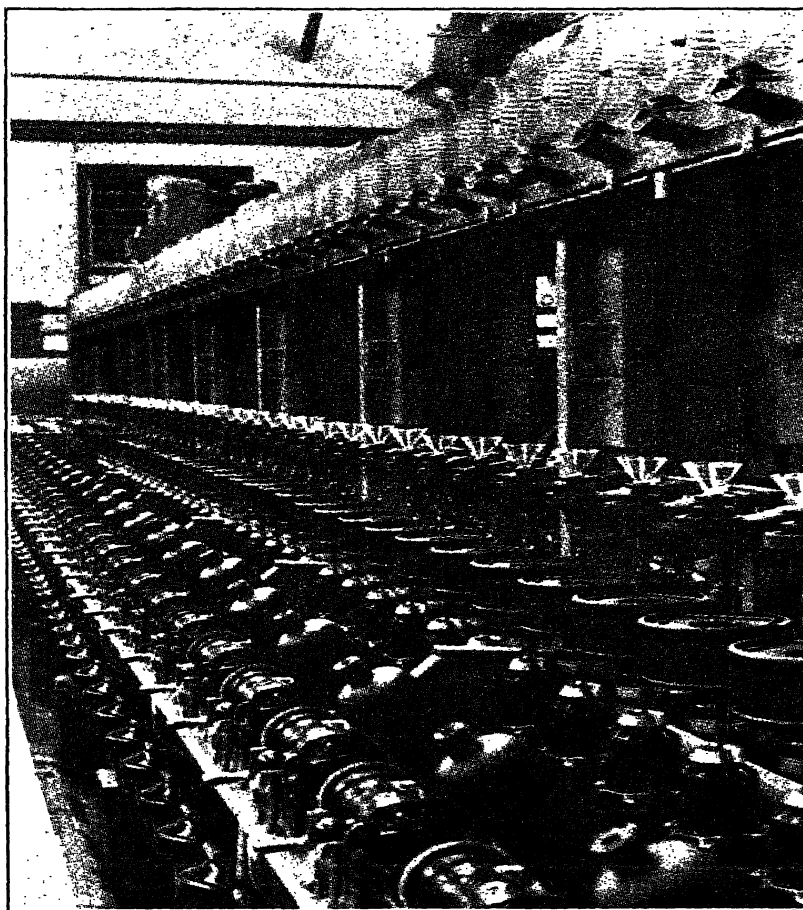
made originally of platinum, and platinum alloys, but now base metal, acid-resisting spinnerets are coming into use more and more. It has a number of symmetrically spaced openings, varying in size, for example, 0.08 mm. in diameter. The number of openings may be 10, 40, 150, or other total, for each spinneret. Each opening forms a filament, which coagulates separately, and all the filaments from one spinneret form a thread. As may be imagined, a very small speck of dirt will suffice to

block an opening and break the thread, hence the supplementary filtration in the candle filter.

Coagulating Bath. As the filaments are ejected from the spinneret, they enter a bath held at 45° C. (113° F.), containing 9 to 11 per cent sulfuric acid, and 20 per cent sodium sulfate. An addition of glucose or other similar substance is made, in order to prevent crystallization, and another one of zinc sulfate (or certain other salts) to promote the crenellation of the fiber. The cellulose is at once precipitated and the bundle of filaments passes under a glass bar, to the "feed wheel," through a glass
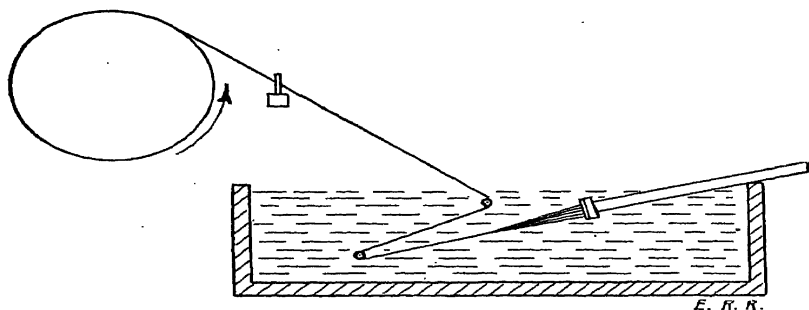
FIGURE 136.—A spinneret for viscose silk.

guide, funnel shaped, to the bucket made of aluminum, Bakelite or Haveg. The action of the acid on the alkali of the viscose produces sodium sulfate which remains in the bath. By circulating to a correcting tank, the composition of the bath may be kept constant. There must be provided for a removal by crystallization of the accumulating sodium sulfate. Not the precipitation only, but also a dehydration, takes place in the acid bath. During the coagulation, part of the sulfur passes out as hydrogen sulfide and is removed by air suction;

$$3CS_2 + 6NaOH = Na_2CS_3 + Na_2CO_3 + 3H_2O, \text{ and}$$
$$Na_2CS_3 + 3H_2O = Na_2CO_3 + 3H_2S$$
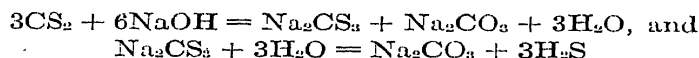
another part remains as elemental sulfur on the fiber. There is tension on the thread from its inception, and that makes for a stronger thread.

The pressure on the viscose at the spinneret is about 25 pounds. The volume ejected from one spinneret is perhaps 10 cubic centimeters per minute. The thread is formed at the rate of 2,500 inches per minute; the bucket rotates at the rate of 7500 R.P.M.; there are three twists per inch of thread. The time the thread spends in the acid bath is one half-second.

Washing and Drying. The wet cake is removed every 4 hours; it measures 5 inches in height and as much in diameter and weighs one pound. To start a new cake, the thread is passed through the stem of the guide with the aid of a little water, a deft operation. The cake is washed with sodium carbonate solution, while hung on white rubber-covered aluminum rods, bleached with chlorine water, perhaps oiled by

TABLE 46.—*Classification in 7 Classes of Petroleum Crudes, According to their "Base," from the Distillation-Analysis of 800 Samples of Crude from All Over the World* [R. I. 3279, U. S. Bureau of Mines, E. C. Lane and E. L. Garton (1935); condensed].

	A Paraffin base oil (wax-bearing)	B Paraffin intermediate base oil (wax-bearing)	C Intermediate Paraffin base oil (wax-bearing)	D Intermediate base oil (wax-bearing)	E Intermediate Naphthene base oil (wax-bearing)	F Naphthene intermediate base oil (wax-bearing)	G Naphthene base oil (wax free)
A.P.I. gravity	49.7°	39.2°	29.5°	39.6°	15.3°	29.5°	24.0°
Specific gravity	.781	.829	.879	.827	.964	.879	.910
Pour point	below 5° F.	below 5° F.	40° F.	below 5° F.	40° F.	below 5° F.	below 5° F.
Per cent sulfur	0.1	0.28	0.32	0.33	3.84	0.16	0.14
Saybolt Universal viscosity 100° F.	34 seconds	41	120	39	4000	47	55
Color	green	greenish-black	greenish-black	green	brownish-black	greenish-black	green
Distillation 1st drop	93° F. (34° C.)	91° F. (33° C.)	176° F. (80° C.)	84° F. (29° C.)	280° F. (138° C.)	138° F. (59° C.)	315° F. (157° C.)
Distillates:							
Gasoline and naphtha	45.2%	32.0	5.8	35.6	2.9	21.3	1.1
Kerosene	17.7%	17.2	nil	4.9	4.5	nil	nil
Gas oil	8.3%	10.6	27.8	17.3	10.6	34.6	55.5
Nonviscous lubricating	9.8%	10.9	20.4	9.4	8.6	10.4	14.2
Medium lubricating	3.4%	5.2	9.2	6.3	0.7	7.0	4.7
Viscous lubricating	nil	nil	nil	nil	1.020	4.7	11.6
Residuum	14.7%	23.5	36.4	22.1	58.4	21.4	12.7
Distillation loss	.9%	.6	.4	1.4	1.9	0.6	0.2
Carbon residue of residuum	1.1%	6.2	6.9	7.3	18.2	8.7	4.5
Carbon residue of crude	0.2%	1.5	2.5	1.6	10.6	1.9	0.6

Key fraction No. 1. (250-275° C.) 482-527° F., 750 mm. pressure.

Per cent cut	6.8%	6.5	7.1	5.8	5.1	10.1	19.6
A.P.I. of cut	44.7°	40.0	36.4	37.0	37.0	30.2	27.9

Key fraction No. 2. (275-300° C.) 527-572° F., 40 mm. pressure.

Per cent cut	4.4	5.7	9.0	4.9	8.2	6.0	7.3
A. P. I. of cut	34.4°	29.3	30.0	24.9	19.5	24.0	16.5
Viscosity at 100° F.	110 seconds	120	120	165	240	230	over 400
Cloud test, in °F.	90	90	90	80	70	90	below 5

If key fraction No. 1 reads 40.0° A.P.I. or lighter, the lower boiling fractions of the oil are paraffinic; if it reads 33.0° A.P.I. or heavier, they are naphthenic; if its gravity lies between 33.0° and 40.0° A.P.I., they are intermediate.

If the gravity of key fraction No. 2 is 30.0° A.P.I. or lighter, the higher-boiling fractions of the oil are paraffinic; if it is 20.0° A.P.I. or heavier, the fractions are naphthenic; while if the gravity lies between 20° and 30° A.P.I., the fractions are intermediate.

FIGURE 138.—The rayon plant at Spruance, Virginia, of E. I. du Pont and Company, as seen from the air (by permission).

running on an oil emulsion, whirled in a large centrifuge to remove all mobile water, and dried in hot closets with circulation (*see* flow sheet). Then the thread is rewound under tension into cone shaped spools, for the knitting trade (socks, stockings, lingerie); it is wound into skeins for the weaving trade, much of it for mixed weaves. After a final inspection, the product is shipped out.

In order to produce 1 ton of salable rayon, there are needed 2 tons of caustic (solid $NaOH$), 1000 pounds carbon disulfide, $1\frac{1}{2}$ tons of sulfuric acid, and 1.12 tons of sulfite pulp.

Important developments are taking place constantly in this field of synthetic fibers. One will be indicated. The thread in the Lilienfeld viscose process is set under tension, in a bath higher in acid, and lower in temperature than the standard; also the viscose is made from a xanthate containing twice the amount of carbon bisulfide usually taken.[5]

THE CELLULOSE ACETATE PROCESS

When 1 part of cellulose (cotton linters) by weight is treated with 4 parts of acetic anhydride in 4 parts of glacial acetic acid, with the addition of 0.05 part of sulfur dioxide in 1 more part of acetic acid, a jelly forms first, then solution takes place within 5 to 6 minutes. This reaction takes place in enameled iron tanks. Another formula calls for 1 part cotton, 3 parts anhydride, and 3 parts acetic acid. To the resulting solution, water is added, and a precipitate appears in the form of white floccules; these are washed from acid, dried, and dissolved in acetone, forming the spinning solution. This latter is filtered with great care, and delivered under pressure to the spinnerets. The liquid thread is ejected downward; a stream of warm air traveling vertically upward, removes the solvent, allowing the solid thread to form. A spinneret made of non-corrosive metals (but not noble metals) is used; it has openings similar in size and number to those in the spinnerets for viscose silk, and the resulting acetate silk is described in terms of deniers and filaments. The thread from the spinneret is wound on a bobbin or forms a cake in a small centrifugal, after which it is twisted if on a bobbin, spooled and reeled into yarn or wound into cones. The acetic acid, partly introduced as such, partly formed in acetylating, is largely recovered.[6]

$$(\text{Cellulose}) \, OH + CH_3 . CO . O . CO . CH_3 = (\text{cellulose}) \, O . CO . CH_3 + CH_3 . CO . OH$$
$$\text{acetic anhydride} \qquad\qquad \text{cellulose acetate} \qquad \text{acetic acid}$$
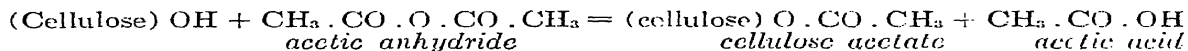
It will be noted that for each hydroxyl in cellulose which is changed into the acetyl derivative, one molecule of acetic acid forms. Of the several hydroxyl groups in the cellulose molecule, only a few are acetylated. A portion of the acetone is also recovered.

The product from this process is not regenerated cellulose, as in the case of viscose silk or rayon; it is an ester of cellulose, cellulose acetate. The ester radical remains in the finished product, which weighs some

[5] *Ind. Eng. Chem.*, **22**, 464 (1930).
[6] *See* Brewster process, Chapter 16.

50 per cent more than the original cellulose taken. It is properly called acetate silk; example of trade names, Acele, Celanese. Originally, acetate silk was much dearer than rayon; by means of improvements, among others a fair recovery of acetic acid, the cost has been gradually lowered.

Acetate silk has a lesser affinity for water, so that when wetted it retains most of its strength, in which respect it is superior to rayon. There is no aging phenomenon to contend with in acetate silk spinning; dyeing is satisfactory; during the process of manufacture, there is a gain in weight. It is likely, therefore, that this process will continue to develop with success. The names of the English chemists Cross and Bevan, and of the Dreyfuss brothers, also Englishmen, are associated with the early developments of the cellulose acetate process.

THE CUPRAMMONIUM PROCESS

The cuprammonium process lends itself to "stretch-spinning." Cotton linters are dissolved in an ammoniacal copper oxide solution; the viscous solution so formed is ejected into water, and the thread formed is stretched, by 40 to 60 per cent, after which it enters the acid coagulating bath and may no longer be stretched. As a result, a thread finer than spun is produced, so that for the very fine filaments (under 100 denier), which possess the greatest softness, this process is well adapted. Other operations are similar those for viscose rayon.

It is not certain, nor is it desirable, that one process should crowd out the others. It is rather more likely that each process will develop a thread with one superior property, strength, capacity for dye absorption, resistance to wetting, evenness, low denier, or some other, so that each process will have a special field and contribution to this new industry.

TABLE 39.—*United States Production of Yarn, by Process, 1935.*[*]

	Pounds	Value	Price per pound
Viscose and cuprammonium	201,964,505	$110,227,777	54.6 cents
Cellulose acetate process	55,592,842	35,839,693	64.0 cents

* Bureau of the Census.

Staple Rayon. A comparatively new product is staple rayon, which has already been mentioned. It is spun as the standard viscose thread, into the same kind of coagulating bath, but a large spinneret or nozzle is used, with, for example, 3200 openings. A thick bundle of threads form, and a number of these are united to form a "rope." After washing, and desulfuring, and drying, the "rope" is cut in short lengths, $1\frac{1}{2}$ inch or 2 inches; these are then blown into a fluffing machine, in which a rapidly revolving wheel separates the threads, leaving them curled and intermixed in all directions. It is packed into bales, very much as clean cotton is. Staple rayon is adapted to weaving on the standard cotton weaving machines. The total cut staple rayon for the world was 271 million pounds in 1936, of which Japan produced 50 million, the United States perhaps 27 million pounds. The price was 35 to 40 cents a pound. The goods made

from woven staple have properties of their own, and are quite different from those made from spun rayon.

Distinction from Worm Silk. Under the microscope, viscose rayon is flat, while worm silk is cylindrical. On burning, viscose rayon and the other forms of rayon give no odor while worm silk emits the odor of burned hair. There are many other tests.[7]

TABLE 40.—*Comparison of the Various Textile Materials Consumed in the United States, 1935.*

	Millions of pounds	Percentage of total
Rayon	251	7.2
Worm silk	62	1.8
Wool	403	11.6
Cotton	2764	79.4

OTHER USES FOR VISCOSE

In addition to rayon, viscose and some of the other cellulose solutions are made into transparent sheets of great brilliance, which are used for wrapping goods of various kinds. Viscose horse hair is used in millinery,

FIGURE 139. — Two handfuls of rayon staple; right, the "rope" cut into 2-inch lengths; left, product after passing the fluffing machine, now similar to cotton in the bale.
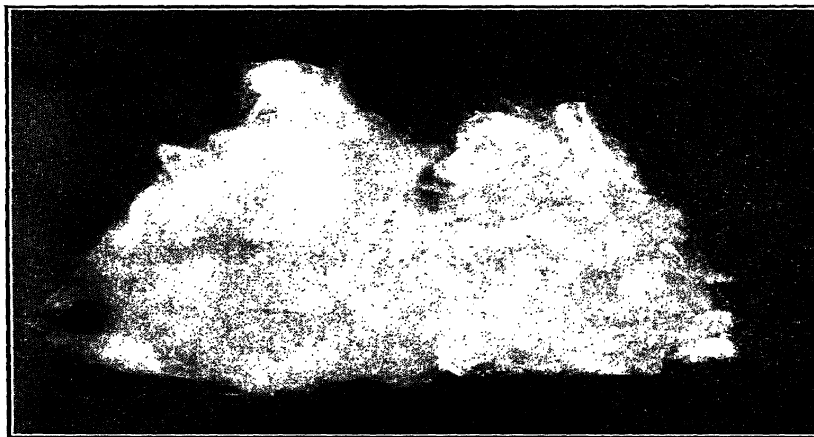
and also artificial straw. A hollow thread has been announced, also cotton fibers coated with viscose, and combinations of rubber and viscose. Wire netting coated with one of the cellulose solutions is suitable as a glass substitute in poultry houses, and offers the advantage of transparency to much of the ultra-violet region of light. (*See* Curves, Chapter 11.)

Hydrated cellulose and cellulose acetate may be formed into caps for sealing bottles. The caps are kept under water until needed. In order to apply a cap, it is placed loosely over the stoppered neck of the bottle and left over night. It shrinks and attaches itself firmly to the neck of the bottle, sealing it.

[7] "Identification of rayon," Wm. D. Grier, *Ind. Eng. Chem.*, **21**, 168 (1929).

Transparent paper (Cellophane, Transparit, Sylphrap) is made by extruding a viscose solution through a long narrow slit into a setting bath. Kodapak is a cellulose acetate sheet of high transparency. The size of the slit determines the thickness the paper will have; the length of the slit is also the width of the paper. The process is continuous, and a sheet of any length is produced. It passes through the setting bath, through water to remove acid, through a bicarbonate solution to neutralize the last traces of acid, through a soda ash solution to remove sulfur, through a dilute acid to remove the carbonate, through water, then through a glycerin solution from which is absorbed 17 per cent glycerin. It is then dried on steam drums and rolled, very much as paper is (Chapter 21). The transparent paper may be colored by passing the paper in the gel state, that is, right after alkali and acid removal, through a dye solution. It may be embossed by passing it between engraved copper rolls.

Cellophane is made moisture proof and water proof by passing the sheet, after the glycerin bath, through a bath consisting of a dilute lacquer solution with rather volatile solvents such as ethyl acetate. The sheet in loop form continues to a chamber wherein warm air removes the solvents; the lacquer with the proper amount of plasticizer and softeners remains as a coating. The solvents are recovered by means of activated charcoal.

An artificial sausage casing is now successfully marketed; it is seamless, and is made in the same way the transparent paper is made.[8]

Cellulose Sponge. A strong, durable sponge is made from viscose, by incorporating Glauber salt crystals of all sizes, placing boxes with the mixture in the coagulating bath, and precipitating the cellulose. Some hemp or other fibrous material may be mixed with the viscose. The blocks so formed are leached with warm water, removing the crystals, which then leave corresponding cavities. An improvement[8a] consists in coagulating with a hot salt solution, which penetrates quickly into the interior of the blocks, and also causes the contained Glauber salt to melt and thus be simultaneously removed. The blocks are cut into square edged pieces, about right for one's hand. They take up water and may be squeezed free from it just like a sponge. A cellulose sponge with uniformly fine cellules is made by using fine crystals exclusively.

VULCANIZED FIBER [9]

Vulcanized fiber is made from cotton and linen rags, not from wood cellulose. The rags are washed, shredded in a beater engine and made into paper in the same way as expressed in Chapter 21. The paper is then passed through a solution of zinc chloride of approximately 70° Bé. concentration. This gelatinizes the paper and permits it to form a homogeneous layer in the following operation, which consists in winding it

[8] Visking Corporation, 4311 Justine Street, Chicago, Ill.

[8a] U. S. Patent 1,909,629, to Hugo Pfannenstiel; earlier patents are 1,142,619 and 1,611,056.

[9] Description written specially for this text by Dr. Gustavus J. Esselen, Cellulose expert, Boston, Mass.

up on a warm, heated, iron roll until the desired thickness has been reached. It is then washed in successive solutions of gradually decreasing zinc chloride content, and finally with water. The washing operation is a time-consuming one and may take anywhere from ten days to two months, depending upon the thickness of the stock. After the zinc chloride has been completely removed, the vulcanized fiber is dried, and is then subjected to a preliminary flattening operation, following which it is calendered by passing it between heavy rolls.

Although the larger part of the vulcanized fiber is now made by the zinc chloride process described above, there is still a certain amount made with sulfuric acid in which a cold acid of about 54° or 55° Bé. concentration is used. With this process, the paper is not ordinarily wound up on a forming roll, but several layers are passed through the acid simultaneously and are combined by running them between a pair of rollers under pressure. The resulting sheet is first run through dilute sulfuric acid and finally washed in water.

Vulcanized fiber is unusually tough and resistant to abrasion, yet it can be readily worked by mechanical means. It finds extensive use for containers such as wardrobe trunks, roller trucks in textile mills, waste baskets, etc., where the material has to withstand hard usage for long periods of time. Its chief drawback is the fact that it absorbs moisture and therefore does not hold its dimensions accurately under changes in atmospheric conditions. For example, if immersed in water for twenty-four hours, it will absorb between 40 and 60 per cent of its weight of water, and swell considerably at the same time.

The usual color of vulcanized fiber is a sort of gray, though it can be readily made in red, black or other colors by the introduction of suitable pigments during the process of making the paper.

Other Patents

U. S. Patent 1,839,773, manufacture of rayon, by aging soda cellulose from wood pulp, converting to cellulose xanthate; 1,790,599, spinning of artificial silk, cellulose acetate especially; 1,770,750, manufacture of artificial silk thread by cellulose process; 1,770,412, spinning viscose by centrifugal, and washing in spinning box (Al) with a dilute hot solution of the salt of a weak acid, with alkaline reaction; 1,702,837, rayon from viscose; 1,756,435, treating rayon to remove detrimental chemicals; 1,871,245, process for making viscose, to serve for rayon and cellophane; 1,841,420, in viscose from xanthate, H₂S liberation prevented by converting the S compounds into non-volatile ones; 1,814,542-3, shortening the time of ripening of viscose by adding hemi-cellulose at some stage of the preparation; 1,779,521, viscose, forming a soluble xanthogenate, and removing S compounds before precipitating the viscose; 1,790,990 (Lilienfeld) viscose from cellulose; 1,990,556, on a rubber funnel thread guide; 2,060,964, funnel for spinning rayon; 1,984,853 and 1,986,813, apparatus for spinning rayon; 2,063,180, production of artificial filaments; Brit. Patent 417,920, on artificial products from viscose; U. S. Patents 1,993,816 and 1,990,617, apparatus for making rayon; 2,024,962 and 2,012,723, on rayon manufacture; 2,018,028, 2,010,822, 1,995,732, 2,022,856, on making cellulose acetate; 2,020,247, cellulose acetate composition and plasticizer; 2,010,111, making cellulose esters; 1,990,113, apparatus for manufacture of cellulose esters.

Problems

1. 100 pounds of cotton linters which contain 98 per cent α-cellulose are to be made into viscose. The batch is treated with 15 per cent NaOH to produce the

alkali cellulose and the latter is churned with 46 pounds of CS_2. Make an estimate of how much xanthate is formed, using the formula in the text for your composition. By means of 8 per cent caustic, this xanthate is extended to make 1250 pounds of viscose. This is spun, and the yield in the form of filaments in thread form is 88 per cent. What is the weight of rayon obtained?

2. For a daily capacity of 10 tons of product, what volume of viscose with 6 per cent cellulose must be handled, the recovery in this case being taken as 96 per cent? What is the number of tanks you must have ready filled with the viscose for one day's supply, for the production just stated? The tanks are upright cylinders, 6 feet in diameter and 10 feet high. The specific gravity of the viscose is 1.11 at 18° C. (64° F.).

3. Sixteen times the original 125 pounds of sulfite pulp, with a content of 86 per cent α-cellulose, 2 per cent β-cellulose, and 6 per cent hemi-cellulose have been made into a viscose with 6.7 per cent cellulose in solution. This viscose also contains 6 per cent NaOH. In spinning this amount, there will be neutralized in the coagulating bath how much sulfuric acid? And what is the weight of sodium sulfate as Glauber salt which must be removed in order to discard the exact increment of this salt by the neutralization process?

4. Let all of the cellulose in the viscose, as per Problem 3, be made into cellophane, without loss. What will be the weight of the cellophane obtained, allowing for a 17 per cent glycerine content, and a 3.5 per cent residual moisture?

5. A batch of cellulose acetate yarn is manufactured, the cellulose acetate corresponding to 240 pounds of cellulose in suitable form. Using the quantity relations in the text, how much acetate yarn will be obtained, assuming no loss and no waste?

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The three foods essential to the well-being of man are proteins (meat), fats and carbohydrates; the most palatable form of the latter, sugar, is found in nature and needs only to be extracted from the plant. Still another form is starch, found in a still greater number of plants, and not extracted for food purposes, as a rule; it is isolated for industrial purposes, and from it, among other things, an artificial sugar is made, which is a food.

Chapter 23

Cane Sugar, Beet Sugar, Corn Starch, and Glucose

The extraction of sugar from the plant, and the refining of the crude extract, are important industries, for sugar is a favorite and practically universal food. It is estimated that the average man in the United States consumes 2 pounds of sugar per week. The white crystalline substance which is usually called sugar, is more correctly designated as sucrose, a disaccharide. The plants in which it occurs and which are used as sources are the sugar cane * and the sugar beet; the former grows in tropical countries, the latter in temperate ones. The method of extraction from the sugar cane is the crushing of the cane and collecting the juice which forms; it is essential to press the canes as soon as cut, for otherwise there is an inversion of sucrose to invert sugar, which represents a loss of crystal sugar. The juice must be concentrated and crystallized in the neighborhood of the plantation, for it contains much water which could not be transported without great shipping expenses. It is customary therefore to work up the cane juice into a first-crystallized sugar in many rather small plants. As this first sugar is still colored, and has an unpleasant odor, it must be refined, and this is best done in a few central plants, the refineries. Hence it is well to distinguish three industries, cane sugar manufacture, cane sugar refining, and beet sugar manufacture, which latter is so conducted that no refining is required. It will be remembered that although the word "manufacture" is used, there is really no manufacture of the sugar, but merely an extraction; the sucrose is already present as such in the sugar cane or beet.

The relative importance of the various sources for sugar in the United States is indicated in Table 41.

Over half of the world's supply of cane sugar is obtained from Cuba, the greatest cane sugar-producing country; the next in importance is Java, whose product furnishes Great Britain with a part of its needs. Of the world production, about half is cane sugar, half beet sugar. Before the war, the production of beet sugar was greater, but during the war it fell off, since Germany, and France and Belgium next, are the

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* The sugar cane originated in India, and was known to the Greeks and later to the Romans; it spread from there, by the agency of man, in succession, to China, Arabia, Tunis, Morroco, Madeira, the Azores, Cape Verde Islands, islands of St. Thomas, Brazil, Jamaica (1656), San Domingo (1697). Cuba experienced the first blooming of its cane cultivation in 1772, although the introduction had taken place many years before; the cane was brought to Louisiana in 1751; it was also carried to Java at that time.

greatest beet sugar producers. The beet sugar industry is gradually regaining its place. Within the United States more beet sugar is produced than cane sugar; the latter comes mainly from Louisiana. The neighbouring Southern States raise a small crop of sugar cane which is

TABLE 41.—*Sources of Sugar (Sucrose).**

	Crop year 1934–35	Crop year 1935–36	Crop year 1936–37
World production	Short tons	Short tons	Short tons
Beet sugar	10,748,000	10,608,674	10,746,799
Cane sugar	20,638,000	20,853,436	22,569,754
Estimated total	29,259,000	31,562,110	33,316,553
Production in Cuba (cane)	2,841,871	2,899,002	3,337,600
(The record is 5,812,068 in 1924-5)			
United States production	Average 1928-32	1935	1936
Beet sugar	1,160,000	1,185,000	1,313,000
Cane sugar	200,000	375,000	397,000
Received from Philippines			985,450
Hawaii			1,032,812
Puerto Rico			909,445
Virgin Islands			3,696
Imports from Cuba			2,102,607
Beet sugar production in			estimated:
Germany	1,855,196	1,847,104	1,918,118
Russia	1,547,078	2,204,600	2,000,000
France	1,347,941	1,010,000	1,030,000

* Selected from figures supplied by the Bureau of Agricultural Economics, Department of Agriculture, Washington, D. C.

made into sugar syrup. The growth of the beet sugar industry, in competition with imported cane sugar, has been rapid, thanks in part to a protective tariff of 2 cents a pound,[1] in part to modern equipment and scientific studies of the culture of the beet.

In the evaluation of sugar, the fact is utilized that sucrose dissolved in water rotates the plane of polarized light to the right; the invert sugar which is formed from sucrose by the action of certain organisms or of acids rotates the plane of polarized light to the left; other impurities have no effect on the polarized beam. Hence the extent of the rotation to the right is a measure of the sucrose content of any solution, or of any solid after dissolving it. The instrument used is the polariscope, or if the readings are marked directly in percentage of sucrose, the saccharimeter. The latter instrument is the more common, and is conspicuous in any sugar laboratory.[2] The reaction for sugar inversion with the degrees of rotation for the pure substance in each case, and the direction of rotation (+ for right or dextro, — for left or levo) is:

[1] The tariff for 75° sugar is 1.7125 cents per pound, with 0.0375 cents more for each additional degree, per pound (U. S. Tariff Act, 1930). Cuban sugar is 96°, hence should pay 2.50 cents per pound; a 20 per cent preferential is applied, however, so that it pays 2 cents. The degree of sugar is obtained by reading the rotation of a beam of polarized light. The magnitude of the rotation is proportional to the amount of cane sugar present. In "direct polarization," the instrument is so arranged, and the amounts of sample and solvent are so chosen, that the degree read is also the percentage of sucrose, without any further calculation.

[2] The polariscope is a half-shadow instrument whose original form is due to Antoine Laurent; *compare* the "Chemiker-Kalender," 1924, or more recent editions, by Dr. Walther Roth, published by J. Springer, Berlin; or other chemists' handbooks.

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6, \text{ hence } \frac{+52.8 - 92.8}{2} = -20.0°.$$

$$\begin{array}{ccc} \textit{sucrose} & \textit{d-glucose} & \textit{l-fructose} \\ +66.56° & +52.8° & -92.8° \end{array}$$
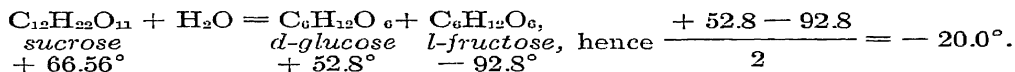
The sum of the rotation of the two mono-saccharides, on the right of the equality sign, is a negative rotation, hence there is an inversion of the sign.[3]   Glucose and fructose are sometimes called reducing sugars, because they reduce Fehling's solution while sucrose does not.
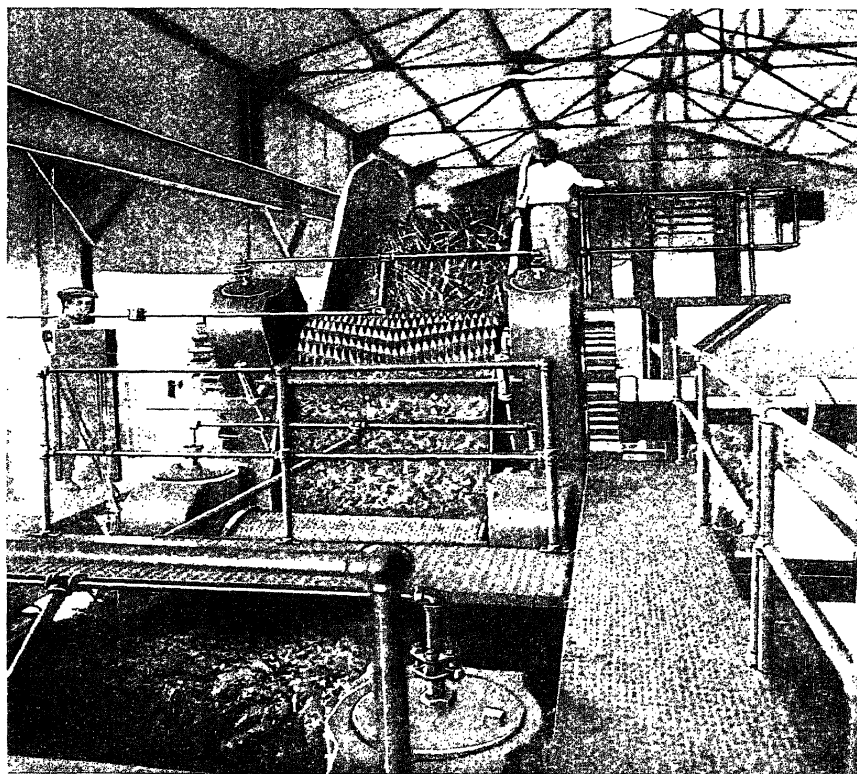
FIGURE 140.—Front view of a sugar cane crushing mill. (Courtesy of Geo. L. Squier Manufacturing Co., Buffalo, N. Y.)

SUGAR FROM THE CANE

The sugar cane is a species of grass, with a single, woody stalk, surmounted by a group of broad leaves; it reaches a height of 18 feet, and is planted from cuttings of specially grown canes called the seed canes. At maturity, the plant develops many very small flowers at the top, forming a tuft.   In harvesting, the cane is cut at the ground, the leaves and tuft removed, and the stalk only carried to the mill.   Because of the

[3] The name invert sugar is due to this inversion of the sign of rotation.

danger of inversion, the cane must reach the crushers in a few hours, so that a mill serves only a limited territory. The sucrose content in the sugar cane varies between 16 and 20 per cent of the total weight.

At the mill (Fig. 140) the canes are first cut into short pieces by the rapidly revolving knives of the cutter, and then pass to one or several three-roll crushers, where the juice is pressed out. The rolls revolve slowly, and have corrugations. In the usual form, one roll surmounts the lower two rolls; the cane travels as indicated in Figure 141, and is carried from one lower roll to the second by the trash plate. If no water is added, the cane is said to be dry-crushed; if water is played on the cane at the second or third set of rollers, it is wet-crushed. The pressed cane is the "bagasse," which is treated further. The juice drops into troughs under the rollers and is strained, warmed to 200° F. (93° C.) and run into settling tanks for a short time.

The bagasse still retains some sugar; in some plants, it is passed through a shallow trough containing water, on an endless belt, and pressed in crushing rolls once more. The dilute solution so obtained may be added to the first juice. The spent bagasse is a sponge-like material; it serves as fuel, sometimes with the addition of crude oil, or fuel oil; as a source of cellulose, or for making Celotex board.
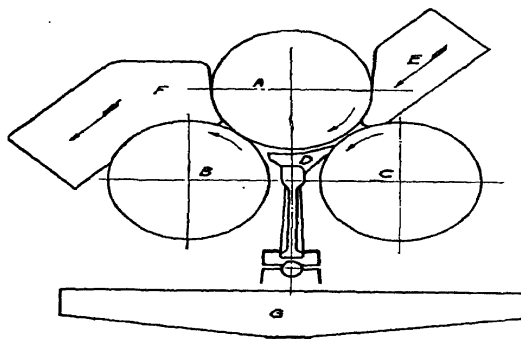
FIGURE 141.—Crushing rolls for sugar cane, with typical turn plate arrangement. *A*, top-roller; *B*, feed roller; *C*, bagasse roller; *D*, trash plate; *E*, feed of cane; *F*, discharge of crushed cane. The juice runs off at *G*. (Special drawing prepared by Geo. L. Squier Manufacturing Co., Buffalo, N. Y., for this edition.)

The amount of juice in the cane varies in different territories; it varies also with the degree of maturity. Of the juice in the cane, 60 to 80 per cent is extracted, depending on the perfection of the equipment. An analysis of the juice follows [4]:

	Per cent
Water	83.6
Sucrose	14.1
Reducing sugars	.6
Undetermined solids	1.7
Total	100.0

Defecation. After any coarse material has settled out, the juice, which is still turbid, and has an acid reaction, is drawn into mixing tanks and

[4] After Spencer, quoted from *U. S. Dept. Agr. Farmers' Bull.* **429, 15** (1911).

treated with enough lime to render it slightly alkaline. The lime precipitates a number of undesirable impurities; the limed juice is warmed by steam, until the precipitate forms a crust (1 hour); the albuminous material coagulates on the lime precipitate and is carried down (or up) with it. After short settling, the clear juice is drawn off to the evaporators. (*See* Fig. 142.) The remaining precipitate is filtered in presses of the plate or of the shell and leaf type,[5] the cake washed somewhat, and used for fertilizer.
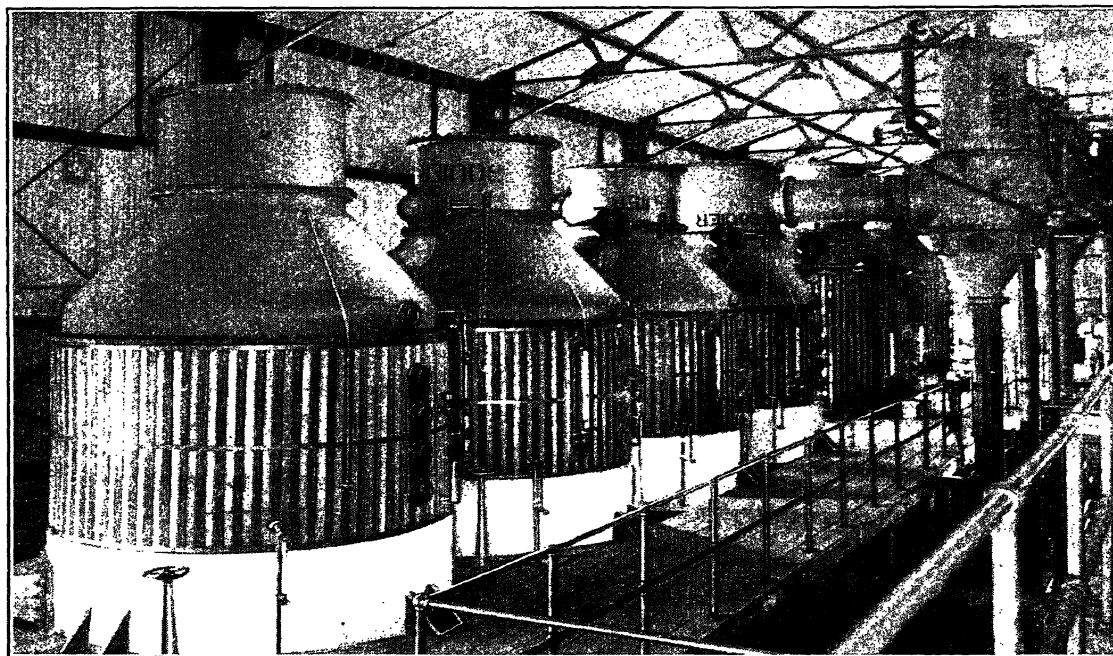
FIGURE 142.—A quadruple effect evaporator, installed in a Porto Rico sugar plant. (Courtesy of the Geo. L. Squier Manufacturing Co., Buffalo, N. Y.

First Evaporation to a Syrup. The comparatively dilute juice, with 14 per cent sucrose, is evaporated first to a strong solution, with about 50 per cent sucrose; such a solution is still clear, but is viscous. This evaporation is generally performed in double- or triple-effect vacuum boilers,[6] in order to save steam.

Second Evaporation to Crystal Formation. The syrup is concentrated further in a single-effect vacuum pan, in which the vacuum and steam may be regulated as the operator deems necessary. In the double-effect for the first evaporation, exhaust steam is used; for the vacuum pan in the second evaporation, boiler steam is used in numerous coils. The syrup is evaporated until a blob on a glass plate examined by lamplight glistens

[5] Chapter 42.
[6,7] Chapter 43.

because of numerous very small crystals which have formed; this is called the graining point. More syrup is then added, in small portions, and the new sugar deposits on the crystals, causing them to grow. This is continued until the desired growth has been attained; the mass in the pan is then the "massecuite," with a total of 82 per cent sucrose, and perhaps 8 per cent water. Of the total sugar, the hot massecuite has 56 per cent as crystals, 44 per cent as solution; after cooling, 65 per cent as crystals, 35 per cent in solution. The thick mass, semi-solid, is placed in centrifugal baskets,[7] the adhering solution whirled off to the envelope, collected and stored as molasses (Fig. 143). The crystals are washed in the basket by clear juice, then removed for shipment. They constitute the raw sugar, which the refineries purchase.
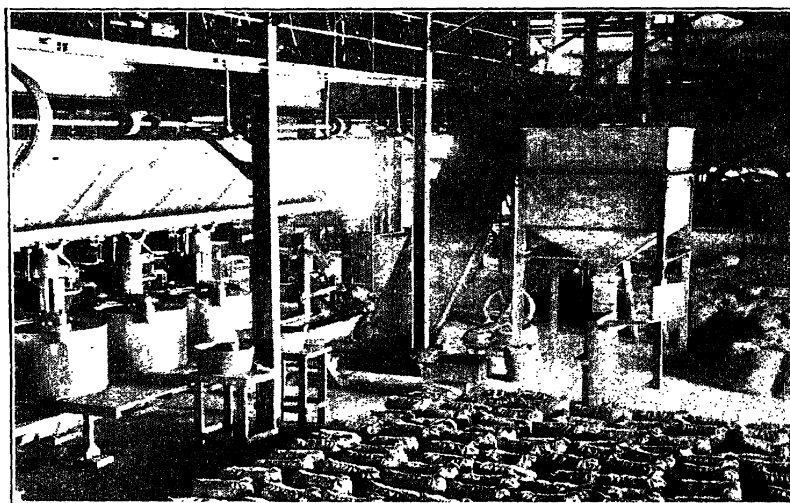
FIGURE 143.—Interior view in a Porto Rico sugar plant, showing the centrifugal machines, on the left, in which the raw sugar is freed from the mother liquor or molasses. This raw sugar is packed in bags for shipment to the refinery, where the white crystal sugar is prepared.

The molasses may be concentrated again, until it contains no more sugar which can be crystallized, when it is sold for cattle food, for the manufacture of industrial alcohol, or other purposes.

CANE SUGAR REFINING

The raw cane sugar generally purchased by the refinery has 95 per cent sucrose; it contains perhaps 1 per cent of glucose, 0.5 per cent ash, and the rest moisture. The main task of the refinery is to remove the color and a slight odor. The raw sugar is mixed with a mother liquor from the previous batch, which removes a large part of the color, leaving the crystals undissolved; these are centrifuged, washed while in the basket, and dissolved with very little hot water to a syrup. A small amount of lime is added, and steam blown in; the suspension is filtered by passing it through bone char in cylinders 20 feet high and 3 feet wide. The filtered

liquor is concentrated to massecuite as was described for raw sugar, centrifuged, and dried in a rotary drier for example to produce granulated sugar. The whole of the white massecuite may be solidified to a loaf, which may be cut into regular cubes or flat pieces (domino sugar). There are many other modifications which lead to special forms.

The bone-char filters are used until they no longer bleach; water is then turned in to remove most of the adhering sugar, the char is dumped and revivified by heating it in absence of air to red heat; it may then be used over again. After a number of such treatments, it loses its decolorizing property and is sold for its phosphate content to the fertilizer trade.

There are simpler ways to purify the sugar; thus mere mixing with a mother syrup, centrifuging, and washing with sugar solutions while in the basket, finally with steam, produces a nearly white product. On the other hand, bleaching by passing sulfur dioxide in the white syrup after lime addition is also practiced, followed by filtering through the bone-char cylinders.

The mother liquors are rather pure, and are usually made into syrups, mixed in some cases with maple syrup.

Sugar from the Sugar Beet

Within the United States, Michigan, Utah, Colorado, and coastal California are the main producers of beet sugar.[8] Thanks to the efforts of European scientists a strain of beets has been developed which produces beets containing as high as 18 per cent sucrose, rivaling the sugar cane.

At harvest time, the beet root, free from the leaves, is carted to the sugar house, washed from dirt, and cut into V-shaped slices about one-quarter of an inch in thickness; these are the "cosettes" or noodles. They are fed to a number of diffusion vessels, so arranged that the noodles may be delivered to any one of the 20 or more vessels from one overhead spout. The extraction is by hot water, in contact with the slices, on the countercurrent principle. Hot water enters the diffuser whose charge is nearly exhausted; sugar diffuses from the cells of the beet into the water; the solution travels to the next diffuser, whose slices are richer. The solution leaving the last diffuser was in contact with a fresh charge. In this way the solution is strengthened until it contains about 12 per cent sucrose, forming a dark solution. The exhausted noodles are washed out of the tank to a receiving box where they dry and are carted away to the farms, to serve as cattle food.

The warm diffusion juice is agitated with 2 to 3 per cent of lime for two hours, after which carbon dioxide is passed in to saturation. The precipitate which forms carries down nearly all impurities; the juice is filter-pressed, and in some plants is treated with lime followed by carbon dioxide a second time, and even a third time. The filtrate obtained is pale yellow; most of this color is removed by sulfur dioxide, which also

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[8] The main producing countries are listed in the introduction. There might be added Czecho-slovakia, the Kief region in Russia, and central Italy.

decomposes some salts of calcium with organic acids, precipitating calcium sulfite. As a rule, the sulfur dioxide treatment follows the first lime treatment. The filtered solution ready for the evaporators is purer than the corresponding solution from the sugar cane. The concentration is performed in double- or triple-effect evaporators, to a clear syrup, as for cane juice, and this is followed by graining in the vacuum pan. The crystals separated by centrifuging are washed in the basket, and after drying, are ready for the market. The mother syrup is concentrated again, giving crystals which are re-worked, and a mother liquor, the molasses. As much sugar is crystallized from the molasses as possible; the remaining sugar is recovered by a chemical process, to give finally crystal sugar for the greater part. In other factories, the molasses is sold as such for consumption. Beet sugar molasses is rarely used for making industrial alcohol.

The sugar in the molasses may be recovered by diluting to about 7 per cent sugar, cooling to 12° C. (53.6° F.), and adding pulverized lime from a Raymond type mill [9] while agitating violently; tricalcium saccharate precipitates. It is filter-pressed and washed and serves instead of lime in the purification of the warm diffusion juice (Steffen process). When this process is used, the total recovery of sucrose in the beet is 85 to 88 per cent.

There is still sugar left in the mother liquor from the Steffen process; it may be recovered by means of the barium saccharate process, successfully operated by a large American beet sugar company. Barium hydroxide is added to the discard molasses; the sugar precipitates as monobarium saccharate, which is filtered, and decomposed by means of carbon dioxide. There are formed barium carbonate, and a solution of sugar which is worked up as usual. The barium carbonate is put through a cyclic process, for the regeneration of barium hydroxide. The carbonate is mixed with sand, or monobarium silicate from a previous run, and furnaced to form dibarium silicate. This latter is suspended in hot water, giving a solution of barium hydroxide and monobarium silicate. The sugar produced by this process is of the highest purity.

Other forms of sugar are sorghum or sorgho syrup (Alabama), maple syrup (Vermont and New York), and honey, at one time of great importance; to these natural sugars, the manufactured glucose, described in the latter part of this chapter, must be added. Another natural sugar which may be produced in quantity in the near future is crystallized levulose from the French Jerusalem Artichoke, which has been grown in Pennsylvania.[10] The tuber contains as high as 12 per cent fructose (levulose), of which 80 to 85 per cent may be recovered in crystallized form. Glucose from starch is presented in this chapter, and "sugar by the hydrolysis of wood cellulose" is part of Chapter 16.

[9] Chapter 44.
[10] *Ind Eng. Chem.*, **16,** 1250 (1924).

CELOTEX

Instead of burning bagasse under boilers, it may be made into a building board called Celotex. The bagasse is freed from gums and waxes and the resulting pulp made into sheets one-quarter inch thick, very much as cardboard is made. After drying, the resulting board is suitable for sheathing buildings, either as outside covering or under clapboards and shingles. It is stronger than wood, and has a high insulating value. A certain amount of sugar clings to the cellulose.

STARCH

Starch, like sugar, occurs as such in the plant and requires only an extraction. Corn is 65 per cent starch; wheat, rye, and rice contain a high percentage of starch; potatoes contain 15 per cent. If a raw potato is grated, and the gratings gently agitated in a tumbler of water, a cloudy liquid forms which, strained from the pulp, deposits a white powder in a short time; this powder is the starch. The process of extraction in every case is essentially as given, but with a great variation of details. Starch is a food; heated with water it partly dissolves, and the solution has adhesive properties, which leads to its use as a size. Hydrolyzed, the large starch molecule $(C_6H_{10}O_5)_n$ gives dextrin or British gum, with a somewhat smaller molecule; maltose, the disaccharide, on continued hydrolysis, and finally, d-glucose, the monosaccharide, discussed under sugar. To some extent, all these products are formed at the same time; on lengthening the process, more dextrin passes into the lower forms; with the longest treatment, all the starch passes into d-glucose.[11] The hydrolysis is hastened by the use of dilute mineral acids, and these are therefore used for the production of commercial glucose, the syrup, from starch; for this manufacture, starch, extracted from the plant, becomes a raw material.

Starch from Corn (Maize) and Corn Oil. In the United States, starch is made from corn almost exclusively.[12] The corn is steeped in water which contains a small amount of sulfurous acid (H_2SO_3), chiefly as a germicide; the softened grain is shredded in squirrel-cage disintegrators,[13] and next suspended in water, with agitation. The corn seed, or germ, floats easily and is run off with a gentle flow of water from the surface of the tank; the hull, starch, and gluten remain in the water and are run off at a lower take-off.

The germs are rich in oil; they are collected, dried, and pressed for the oil in a way very similar to the pressing of flaxseed for linseed oil [14]; the product is corn oil. The press cake serves as a cattle food.

[11] The old name for dextro-glucose, namely dextrose, has become irrational since the synthesis of levo-glucose, and should therefore be abandoned.

[12] In 1914, 97.4 per cent of the starch made was from corn, 1.6 from potatoes, 1 from wheat. In Germany, potatoes are the usual source (U. S. Tariff Commission, *Tariff Information Survey* G 14, 1921, p. 14); in 1929, 93 per cent of the starch made was corn starch (U. S.), and in 1935, 90.7 per cent.

[13] Chapter 44.

[14] Chapter 29.

The suspension containing the starch is screened through bolting cloth stretched on a frame of wood to form a cylinder, which slowly revolves about its long axis; starch and gluten pass through, the hull is retained. The starch suspension is next passed through a long shallow trough slightly inclined at the far end; the starch grains settle in the trough, while the gluten floats off. The separation is not perfect; even after repeating it the gluten still contains a large percentage of starch. The gluten is made into gluten meal (filter press) for special breads.

The starch in the troughs or runways is shoveled onto small cars, washed again for certain grades, settled and dried at a low temperature.

GLUCOSE

In order to change the starch to the commercial glucose, the syrup, it is hydrolyzed with a 0.5 per cent sulfuric acid solution; in Europe, hydrochloric acid is generally used. The starch is suspended in much water, the acid added in a preliminary, open converter, and the whole heated with steam; after an hour, it is transferred to the closed converter, of copper, and heated further by direct steam under a pressure of 50 pounds; the time in the second converter varies from 10 to 20 minutes. The discharged product is neutralized with soda ash; impurities separate in the neutral solution, are filtered, and the clear filtrate is passed through bone-char filters. A second filtration is followed by an adjustment of the p_H of the glucose syrup to 4.7, by means of a small amount of hydrochloric acid (never exceeding .0047 per cent), a reconcentration to proper gravity, and neutralization of the mineral acid by sodium acetate, leaving the p_H at the proper figure. This is done to prevent inversion of cane sugar when the syrup is mixed with it in confectionery manufacture. The final syrup is about 45° Bé. and is clear and colorless.

Commercial glucose is not a single substance in solution, but a mixture of three: dextrin, maltose, and glucose. The bulk of the syrup on the market contains about 34 per cent of reducing sugar, essentially glucose, and calcu ated as such. It serves in the confectionery trade as a sweetening agent; it is also sold in small cans for consumption as a syrup in households.

By using more acid and heating in the closed converter for a longer period (30 minutes), the conversion to glucose is approximately complete. A starch solution rotates polarized light farther to the right than d-glucose; the fall in rotation has therefore become a means of following the progress of the conversion. The product after neutralization and filtration may then be made into a solid, by evaporating in two steps, as with cane sugar. In the first step, the syrup is produced, and this enters a single-effect vacuum pan, where it is concentrated to 42° Bé., with a content of 80 per cent glucose. The concentrated sugar liquor is run onto large tables where it solidifies; when cold, it is cut into slabs, and these are chipped into smaller pieces for shipment. This is corn sugar, also called grape sugar. It may be crystallized by seeding it with glucose

crystals, called dextrose in the trade. The sugar is slowly agitated during crystallization, which is slow; after 90 to 100 hours, the crystals are centrifuged, and are then 99.5 to 100 per cent pure. This is dextrose hydrate, perfectly white in color.

The syrup from the first step is "corn syrup unmixed" used in candy making, in baking, preserving; with the addition of cane sugar syrup, it becomes a table syrup, known for example as Karo syrup.

Both corn syrup and corn sugar are of industrial importance, as indicated in Table 42.

TABLE 42.—*Products from Corn in 1935 (U. S.).*

	Pounds	Cents per pound
Starch from corn	756,281,202	3.52
Corn sugar	351,084,860	3.14
Corn syrup, unmixed	783,959,169	2.71
Corn oil	127,394,939	10.82
Corn oil cake and meal	19,325 tons	$23.40

*Bureau of the Census.

OTHER PATENTS

1,849,998, production of sugar from dried sugar beet; 1,755,165, method of treating beet juice to produce sugar; 1,750,756, manufacture of corn starch; 1,792,088, manufacture of soluble starch, by sodium hypochlorite.

PROBLEMS

1. During the harvest, 1000 gallons (sp. gr. 1.06) of cane juice is crystallized every day. The analysis is as given in the text. The recovery of sucrose is 65 per cent; the raw sugar separated contains 95 per cent sucrose. How many pounds of raw sugar will be obtained per day? What size tubs would you select for holding the juice?

2. Two tons of sugar beet containing 16 per cent sucrose are extracted. The recovery is 80 per cent. How many pounds of beet sugar are obtained? In order to precipitate the remaining sucrose, hydrated lime is added to the molasses, in an amount sufficient to precipitate all the sugar as tricalcium saccharate $3CaO . C_{12}H_{22}O_{11}$. How much lime will you need?

READING REFERENCES

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"Cane sugar and its manufacture," H. C. Prinsen Geerligs, London, Norman Rodger, 1924.

"Cane-juice liming and clarification." R. H. King, *Ind. Eng. Chem.*, 23, 954 (1931).

"The celotex and cane-sugar industries, bagasse or sugar a by-product?" E. C. Lathrop. *Ind. Eng. Chem.*, 22, 449 (1930).

"Outline of the activities at Argo," published by the Corn Products Refining Company, Argo, Illinois.

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In 1936, there were produced in the United States 1,089 million barrels of crude oil, and from these, 19,790 million gallons of gasoline. These figures show that petroleum and its products are necessities in the modern world. It is to the chemical engineer that the world owes the increased amount of gasoline, manufactured in part by "cracking" heavier fractions, in part by polymerizing waste gases; to him it owes the rescue of lubricating oil of the best quality from inferior lube fraction, and the gradually lengthening of the list of products made from petroleum. It is to the geologist and the geophysicist that the world owes new methods of locating oil-bearing rocks.

Chapter 24

Petroleum and Its Products

When first obtained from the ground, before refining in any way, petroleum (rock-oil) is called "crude oil." It shows itself in some cases at the surface, through seepage; in other cases it occurs at moderate depths; in still other cases it must be sought by drill holes 5000 feet and more deep. When such a drill hole reaches an oil basin, the oil is frequently forced out under enormous pressures; gas, salty water, and sand usually accompany the oil. After a period which varies considerably, the flow becomes quieter; after some months it does not gush at all, and the oil must be pumped out; finally, no oil is obtained even by pumping; the well is dry. New wells are therefore constantly sought. The oil prospector chooses lands possessing a subsoil which has characteristics indicating petroliferous strata; these characteristics vary in the various fields, and in no case is it beyond doubt that a drill hole will reach oil. The scientific search for oil is supplemented by accidental discoveries, in the course of drilling for water for example. Where natural gas occurs, it is reasonable to prospect for oil;[*] it is by no means certain that oil will be found, but since petroleum consists of a mixture of hydrocarbons, the lighter ones such as methane, CH_4, and ethane, C_2H_6, may have escaped, leaving the main body of liquids and solids not very far away. The heaviest hydrocarbons are solid; the intermediate ones liquid.

Discovery of Oil. It was not so much the genius of man which discovered petroleum oil, rather was it the oil which revealed its presence and forced itself upon his attention, by seepages which frequently coated small rivers, as in Pennsylvania; by contaminating brines, much to the disgust of the early (1806) salt refiners, as for the brothers Ruffner along the Kanawha river in West Virginia; in the escaping gas rich in vapors and known for centuries, as in the Baku peninsula, where the "eternal" fire gave a powerful support to religious cults (Zoroasters).[1] Only in more recent times, especially in the two decades past, has a more inten-

[*] The Rodessa field, Gaddo Parish, in Louisiana, was a gas field for many years; only in 1935 was it discovered to carry oil.

[1] P. 478 and 474, in "Outstanding features of petroleum development in America," by David White, *Bull. Am. Assoc. Petroleum Geologists*, **19**, 469–502 (1935).

sive search taken place, partly because the evident clues had been exhausted, and partly because petroleum has become a necessity to national as well as to civil life. To the study of the soil for indications of petroliferous strata, which has already been mentioned, there were added scientific methods, the revival of the anticlinal theory, the measurement of temperature in adjacent wells in order to locate the anticlinal axis, gravitometry, including seismic or sonic apparatus, and the magnetometer.[2] Of these a few words might be said in description of the seismic method, the most successful one.

The seismic method for underground exploration is an adaptation of the study of low-lying, deeply buried rock formations, by the echo characteristics of time and direction of an artificial vibration, such as the explosion of a charge of dynamite; it is called the seismic reflection method. A portable seismometer is set firmly on hard ground; it consists of a post bearing a long pointer rigidly fastened to it, and a heavy weight suspended from an arm. The post moves with the vibrations of the ground; the pointer magnifies them, and throws a point of light on the face of the weight. This latter by virtue of its inertia does not respond to the vibrations. A moving picture camera, set in rubber, records the path of the light; the rate of travel of the film gives the measure of time in thousandths of seconds. A charge of dynamite, let us say 11 pounds, at a depth of 95 feet is set off, and the first vibration as well as the subsequent reflections from the low-lying rock formation recorded. The time for the reflection to travel upward gives the depth; thus, in one case, two and 365/1000ths seconds indicated 18,000 feet. The slope of the strata is given by the shape of the curve. Many such records are made in order to plot an area.[3]

Petroleum is found only in sedimentary rocks, and has its origin in the remains of plants and animals,[4] which accumulated along with clays and muds along the sea. At a later geologic period, these strata were lifted and warped, forming arches (anticlines) and troughs (synclines), from one mile to several miles in width. Oil is found in the anticlines, having risen above the water; it may also be found in synclines, if the upper space (to the neighboring anticlines) is filled with the still lighter gas, also formed from these deposits, and tapped as natural gas.

Since 1850, there were manufactured from fatty coals, Scotch boghead, bituminous shale, several products, one of which was an oil used for lighting and called "coal oil," which was taking the place of the disappear-

[2] *Ibid.*, 501.

[3] In part from a radio broadcast by Dr. John P. Buwalda, California Institute of Technology, in a series on Recent Developments in the Geologic Sciences, under the name "Searchers of the Unknown," Jan. 4, 1936.

[4] There have been many theories for the formation of petroleum deposits in the ground. Among the earlier ones was that of Engler who referred the formation of petroleum to a store of fatty remains of all kinds of life, but especially animal life; his opinion was based on laboratory experiments with menhaden oil, from which he produced a petroleum-like substance. C. Engler, *Ber. Deutschen Gesellschaft*, 21, 1816 (1888). Among the present workers, Alfred Treibs assigns to plants the dominant rôle in forming petroleum, to animal remains a secondary rôle. His statement is based on the spectroscopic study of the light absorption of petroleums, in which he thus identifies and estimates quantitatively porphyrins of chlorophyll origin in a high percentage, while he also finds porphyrins of hemoglobin origin, but in much smaller amounts. *Ann.*, 510, 42 (1934). A brief summary of the older theories will be found in "The examination of hydrocarbon oils and saponifiable waxes," D. Holde, tr. by Edward Mueller, New York, John Wiley and Sons, 1922.

ing whale oil distillate. It was for the purpose of securing raw material for such "coal oil" that Colonel Drake sank his now famous well at Titusville, Pa., in 1859; it was 69½ feet deep. Since then oil wells have multiplied; in the United States there were drilled, in 1936, 25,000 wells, of which 18,000 were productive. In 1935, a total of 340,990 wells were productive and in operation (in U. S.); the average yield per well was 8.1 barrels, but while some wells produced half a barrel, others gave 175 barrels per day. When first tapped, the well may be a gusher, with many thousands of barrels per day; this output begins to decrease at once, and gradually tapers off until a pump is needed to bring up the oil. A life of 20 years is the rough estimate for a new pool.

A depth of 4000 feet was considered extreme not so long ago; to-day, 10,000 feet is not unusual.[5] The cost for a 4000-foot well is close to $50,000; for the 8000- and 10,000-foot well, it is $250,000 and more. Depth drilling has been helped by the development of rotary drilling; several new chemical agents and the application of acids have contributed.[6] The world's deepest producing well [7] is 10,569 feet deep (January, 1937).

Petroleum Reserves. Taking petroleum from the ground means taking from a finite store, and at the rising rate of crude oil production,

TABLE 43.—*Estimate of Proven Reserves of the World on January 1, 1936 (in Barrels of 42 Gallons).*

United States**	10,575,000,000
Russia	2,830,000,000
Iraq	2,475,000,000
Iran	2,150,000,000
Venezuela	1,350,000,000
Roumania	633,000,000
Dutch East Indies	450,000,000
Mexico	420,000,000
Columbia	275,000,000
Peru	138,000,000
British India	111,000,000
Argentina	92,000,000
Trinidad	91,000,000
Other countries	375,000,000
World Total	21,965,000,000

* Garfias and Whetsel, Foreign Oil Department, H. L. Doherty and Co., in *Oil Weekly*, 10, (Feb. 24, 1936).

** For the United States, there has been discovered in 1936, an additional 1,088,981,000 barrels. (*Oil and Gas J.*)

thought has been given to the extent of this store. For the world, by countries, the proven reserves, that is, those established by drilling to the pool to establish its dimensions, are given in table 43. For the United States, the relation between proven reserves and production over a period

[5] In some cases, it is possible that an upper pool, which has been pumped out, is underlain by a lower pool. The Fox pool, Oklahoma, at the 2000-foot level, producing since 1916, was "on the pump" in 1935; in October of that year a new well, 8088 feet down, brought in a new producing pool, 6000 feet under the original one. It was gusher, with 8 to 10 thousand barrels a day. "The field that came back," C. E. Savage, *The Lamp*, February, 1936.

[6] "Science goes down an oil well," J. Arthur Sohn, *The Lamp*, December, (1936).

[7] McGonigle No. 12, Ventura Avenue field, California. The record before that was held by Rigolette No. 5, Lafitte field, Jefferson Parish, La., with a depth of 10,244 feet.

of years is shown in the graph adjoined, Figure 144. It would appear that the rate of discovery has kept pace with the rate of production. For 1936, for example, there were added to the proven reserves 1,088,981,000 barrels, just equal to the production. And yet, the possibility of exhaustion after several decades exists. One means for conserving is to reduce or abolish waste, and that is being done by state regulations, by proration, by the unit operation of pools.[8] Another means is the more complete extraction of the oil sands for their oil; it must be explained that the oil nearly always lies in sand, and that rarely is there as much as 50 per cent of the total oil lifted to the ground; more often 30 per cent

FIGURE 144. — A graph showing accumulated discoveries, p r o v e n reserves, and accumulated production of c r u d e oil, in the United States. (From the graph in Bull. Am. A s s o c. Petr. Geologists. **20**, 15, (1936), extended by means of figures from Oil and Gas Journal.)
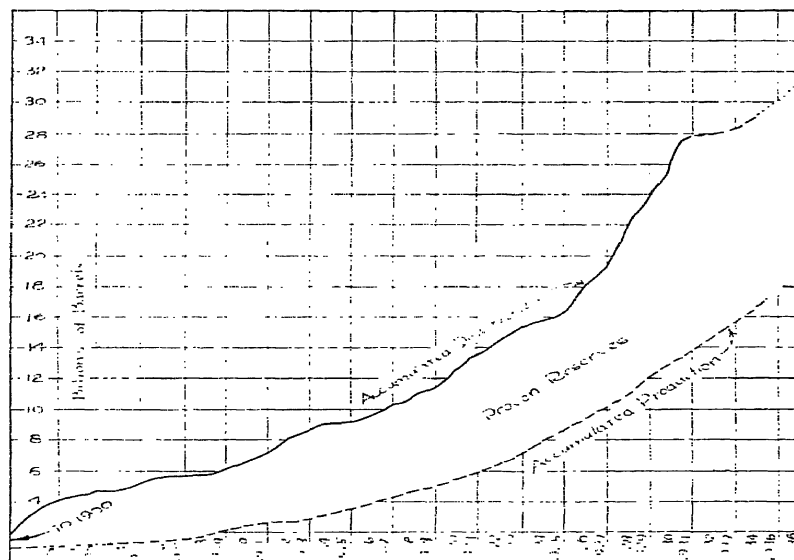
and less. To recover such residual portions of the oil, or at least much of it, flooding by water has given good results in Pennsylvania, but it must be added, poor results in Ohio.[9] The ground formations must be favorable. Another means is the maintenance of reservoir pressure by returning gas or feeding in air under pressure to the formation. The actual mining of the residual sands has been envisaged.

The oil fields in the United States are among the most important in the world. In many localities, oil derricks dot the landscape, as on the way from Pittsburgh to Wheeling, W. Va.; in Los Angeles, there is an oil field within the greater city limits; further north, in the Ventura field, some of the derricks are built over the sea. The relative importance of the several producing States is best shown in Table 44.

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[8] A brief treatment of laws and regulations concerning crude oil production will be found in *Minerals Yearbook*, **674–5**, (1936); *Minerals Yearbook*, **771–794**, (1935). On conservation in general, read: "Probable petroleum shortage in the United States and methods for its alleviation," L. C. Snider and B. T. Brooks, *Bull. Am. Ass. Petroleum Geologists*, **20**, 15 (1936).

[9] See graph on p. 31 *Bull Am. Assoc. Petro. Geologists* **20**, (1936).

TABLE 44.—*Production of Crude Oil in the United States by States, Arranged in the Order of the 1936 Figures, in Thousands of Barrels of 42 U. S. Gallons.**

	1936	1935	1934
Texas	424,396	391,592	378,233
California	214,756	207,832	175,508
Oklahoma	200,881	182,597	178,652
Louisiana	80,807	50,287	32,478
Kansas	57,084	53,364	45,754
New Mexico	26,647	20,154	16,439
Pennsylvania	17,041	15,899	14,572
Wyoming	14,269	13,238	12,489
Michigan	11,977	15,790	10,566
Arkansas	10,697	11,139	11,359
Montana	5,798	4,367	3,509
Kentucky	5,638	5,324	4,868
New York	4,626	4,241	3,814
Illinois	4,439	4,351	4,472
Ohio	3,837	4,121	4,299
West Virginia	3,814	3,959	4,133
Colorado	1,612	1,556	1,130
Indiana	792	767	816
Tennessee	0	0	11
Others	0	43	0
Total	1,089,114	990,621	903,104

* The Oil and Gas Journal, Tulsa, Oklahoma, Jan. 28, 1937, p. 43.

Valuable oil regions occur in Russia, in the Baku peninsula in the Caspian Sea, in Roumania, Galicia, Mexico, Venezuela, and the Dutch East Indies. The production for the several countries is given in Table 45.

Transportation of Crude. In the United States, much of the crude oil is refined in refineries situated near the wells, so that its transport is fairly easy, namely, by pumping. Crude oil is, however, also sent great distances without having to be hauled over the railway; if the freight bills had to be added to the cost of the oil, the petroleum products would be more expensive than they are. The crude oil travels through especially constructed pipe lines laid in the ground along a purchased right of way, in sections 75 miles long or longer. The right of way is patroled for leaks and each section has storage tanks and a pumping station. For Buffalo, the preceding station is Olean, N. Y., where the oil enters a 6-inch line under a pressure of 400 pounds.[10] When a ridge must be crossed the line is so constructed that one leg is downhill so that by its syphon effect it will help pull the oil up the hill. In this way crude oil from Oklahoma reaches Bayonne, N. J., and Marcus Hook, Pa., while Texas crude can be sent to Chicago (Whiting, Ill.) or Buffalo, N. Y. No pipe line crosses the Rocky Mountains.[11]

Formerly oil was burned as such for its fuel value, and to a small extent this is still done; but, by far the greater amount is refined, and

[10] The line is 69 miles long. In spite of a reduction to 4 inches for the last half-mile, a delivery of 7200 barrels for 24 hours was made in July, 1926.

[11] A map of the oil pipe lines may be obtained from the *Oil and Gas Journal*, Tulsa, Okla., for a nominal price. The same map on its other side shows the trunk natural gas lines.

only that portion which cannot be made to yield any of the more valuable products is burned under boilers (fuel oil, bunker oil). On distilling crude oil, there are obtained: gases, which are usually burned under boilers; gasoline, for internal combustion motors with spark firing; solvent naphtha; kerosene, gas oil, fuel oil, lubricating oil, paraffin wax (hard wax), petrolatum (soft wax), road tar, coke, and other products. A selected part of the fuel oil becomes Diesel oil.

TABLE 45.—*World Crude Oil Production for the Year 1936 (Estimated) in Barrels of 42 U. S. Gallons.**

		Per cent of total
United States	1,089,014,000	61.1
U. S. S. R.	193,000,000	10.9
Venezuela	153,315,000	8.6
Roumania	66,100,000	3.7
Iran	62,850,000	3.5
Dutch East Indies (incl. British Borneo)	51,800,000	2.9
Mexico	40,300,000	2.3
Iraq	30,600,000	1.7
Colombia	18,756,000	1.1
Peru	17,320,000	1.0
Argentina	14,950,000	.84
Trinidad	13,400,000	.76
British India (Burma)	9,600,000	.54
Poland	3,600,000	.2
Bahrein Island	3,600,000	.2
Germany	3,300,000	.2
Japan	2,400,000	.14
Equador	1,900,000	.1
Canada	1,507,000	.08
Egypt	1,155,000	.07
Others	1,300,000	.07
Total	1,779,767,000	

* The Oil and Gas Journal, Tulsa, Oklahoma. The 1936 production is a record, up to that year; the 1929 figure was 1,485,867,000 barrels.

Classification of Crudes. An eminently satisfactory classification of crudes has been developed by the U. S. Bureau of Mines; the main features are given in Table 46. Class A comprises the paraffin base crude, which are wax-bearing; this crude contains mainly paraffinic hydrocarbons in all its fractions; its residue in the still becomes the much-sought after "cylinder stock." Straight distilled gasolines from this crude would be paraffinic, and have "knocking" properties. Naphthene base oil, class G, contains mainly naphthenes, that is, cyclic compounds which are saturated, with sidechains both naphthenic and paraffinic. Naphthene base and intermediate naphthene base, class E, may contain much black brittle, almost infusible asphaltic material, although they often do not; when they do, they fit the old description of asphalt base oils. Naphthenes are hydrocarbons of the C_nH_{2n} series, rich in hydrogen, with ring formation; they carry side chains (not shown below) which may be naphthenic

TABLE 46.—*Classification in 7 Classes of Petroleum Crudes, According to their "Base," from the Distillation-Analysis of 800 Samples of Crude from All Over the World* [**R. I. 3279**, *U. S. Bureau of Mines, E. C. Lane and E. L. Garton (1935); condensed*].

	A Paraffin base oil (wax-bearing)	B Paraffin intermediate base oil (wax-bearing)	C Intermediate Paraffin base oil (wax-bearing)	D Intermediate base oil (wax-bearing)	E Intermediate Naphthene base oil (wax-bearing)	F Naphthene intermediate base oil (wax-bearing)	G Naphthene base oil (wax free)
A.P.I. gravity	49.7°	39.2°	29.5°	39.6°	15.3°	29.5°	24.0°
Specific gravity	.781	.829	.879	.827	.964	.879	.910
Pour point	below 5° F.	below 5° F.	40° F.	below 5° F.	40° F.	below 5° F.	below 5° F.
Per cent sulfur	0.1	0.28	0.32	0.33	3.84	0.16	0.14
Saybolt Universal viscosity 100° F.	34 seconds	41	120	39	4000	47	55
Color	green	greenish-black	greenish-black	green	brownish-black	greenish-black	green
Distillation 1st drop	93° F. (34° C.)	91° F. (33° C.)	176° F. (80° C.)	84° F. (29° C.)	280° F. (138° C.)	138° F. (59° C.)	315° F. (157° C.)
Distillates:							
Gasoline and naphtha	45.2%	32.0	5.8	38.6	2.9	21.3	1.1
Kerosene	17.7%	17.2	nil	4.9	4.5	nil	nil
Gas oil	8.3%	10.6	27.8	17.3	10.6	34.6	55.5
Nonviscous lubricating	9.8%	10.9	20.4	9.4	8.6	10.4	14.2
Medium lubricating	3.4%	5.2	9.2	6.3	0.7	7.0	4.7
Viscous lubricating	nil	nil	nil	nil	1.020	4.7	11.6
Residuum	14.7%	23.5	36.4	22.1	58.4	21.4	12.7
Distillation loss	.9%	.6	.4	1.4	1.9	0.6	0.2
Carbon residue of residuum	1.1%	6.2	6.9	7.3	18.2	8.7	4.5
Carbon residue of crude	0.2%	1.5	2.5	1.6	10.6	1.9	0.6

Key fraction No. 1. (250-275° C.) 482-527° F., 750 mm. pressure.

Per cent cut	6.8%	6.5	7.1	5.8	5.1	10.1	19.6
A.P.I. of cut	44.7°	40.6	36.4	37.0	37.0	30.2	27.9

Key fraction No. 2. (275-300° C.) 527-572° F., 40 mm. pressure.

Per cent cut	4.4	5.7	9.0	4.9	8.2	6.0	7.3
A. P. I. of cut	34.4°	29.3	30.0	24.9	19.5	24.0	16.5
Viscosity at 100° F.	110 seconds	120	120	165	240	230	over 400
Cloud test, in °F.	90	90	90	80	70	90	below 5

If key fraction No. 1 reads 40.0° A.P.I. or lighter, the lower boiling fractions of the oil are paraffinic; if it reads 33.0° A.P.I. or heavier, they are naphthenic; if its gravity lies between 33.0° and 40.0° A.P.I., they are intermediate.

If the gravity of key fraction No. 2 is 30.0° A.P.I. or lighter, the higher-boiling fractions of the oil are paraffinic; if it is 20.0° A.P.I. or heavier, the fractions are naphthenic; while if the gravity lies between 20° and 30° A.P.I., the fractions are intermediate.

or paraffinic. The paraffins are the straight chain, or branched chain hydrocarbons; iso-octane, normal heptane, cetane, presented further on

```
        CH₂                          CH₂    CH₂
       /   \                        /   \  /   \
    H₂C    CH₂                   H₂C    CH   CH₂
     |      |                     |      |     |
    H₂C    CH₂                   H₂C    CH   CH₂
       \   /                        \   /  \   /
        CH₂                          CH₂    CH₂
  Hexahydrobenzene              Octahydronaphthalene
    a naphthene                     a naphthene
```
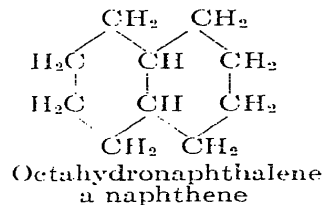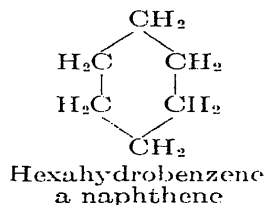
are examples. The naphthenes merge into oils rich in aromatics, that is, derivatives of benzene and higher members of the series C_nH_n, again with an endless assortment of side chains.

The crudes differ also in the relative amounts of lower and higher-boiling constituents; some are so thick that they barely pour; others are as fluid as kerosene. This is well brought out in Table 46; in fact, one of the purposes in giving it is to answer precisely the question: how much gasoline does crude oil contain? The amount varies, but definite figures are now presented. An overall yield will be found elsewhere in the chapter.

The greatest demand is for gasoline, and in order to increase the supply of this material, the higher-boiling hydrocarbons are heated to an excessive temperature which causes their decomposition into more volatile, lower-boiling hydrocarbons, such as compose gasoline; the operation is called "cracking," namely, into smaller molecular fragments.

Exact boiling points and densities cannot be given, but the following may serve as guides:

Gasoline has a density of 55-60° Bé., and boils at 100-400° F.* (37.8-204° C.)
Kerosene has a density of 40-45° Bé., and boils at 400-600° F. (204-315° C.)
Fuel oil varies greatly; it is sometimes 36-40° Bé.
Lubricating oils have a density of 28° Bé., for the lightest engine oil, to very high densities.

    * Bé. scale here is the scale for "lighter than water," *see appendix.*

The older refining units are crude oil stills which separate the raw material into a crude gasoline fraction, a crude kerosene, an intermediate fraction, and a paraffin oil fraction; coke is left in the still, to be knocked out by hand. The operation is discontinuous, and cracking is done in

Origin of samples in Table 46:

A. West Virginia, Ritchie Co., Lost Run field
B. Oklahoma, Lincoln Co., Chandler field
C. Louisiana, Webster Parish, Cotton Valley field
D. Oklahoma, Seminole Co., Seminole field
E. Wyoming, Park Co., North Sunshine field
F. Texas, Austin Co., Raccoon Bend field
G. Texas, Refugio Co., Refugio field

Each of these samples is typical of the class it represents. The seven classes listed in the table are:

A: Paraffin base; distillates paraffinic throughout
B. Paraffin-intermediate base: light fractions paraffinic, heavy fractions intermediate
C. Intermediate-paraffin base: light fractions intermediate, heavy fractions paraffinic
D. Intermediate base: distillates intermediate throughout
E. Intermediate-naphthene base: light fractions intermediate, heavy fractions naphthenic
F. Naphthene-intermediate base: light fractions naphthenic; heavy fractions intermediate
G. Naphthene base, distillates naphthenic throughout.

separate stills.[12]　The preferred method to-day is the continuous pipe furnace with fractionating tower.　The new method makes full use of the fractionating tower for the separation of the various fractions, which are taken off at various levels.　A few general considerations regarding such "bubble towers," as they are called in the oil trade, are in order.

The Bubble Tower.　In a normal column, only one well-fractionated cut can be made; it comes off overhead.　The number of plates fixes the quality of the overhead product.　Refluxing, that is returning to the column of a portion of the condensed distillate, has the effect of reducing the number of plates necessary for a given separation; the greater the reflux ratio, the smaller the number of plates required.　The place to put back reflux is where the composition of the liquid on the plate is the same
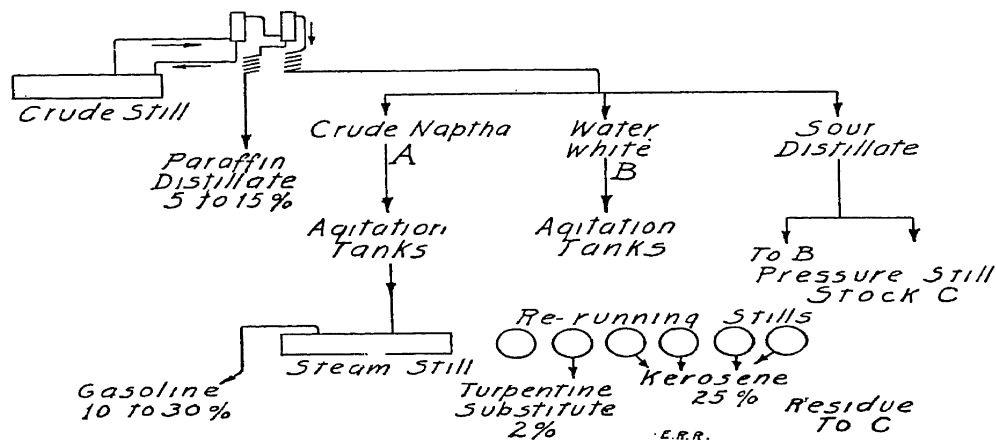
FIGURE 145.—The separation of a crude into the main products, in a batch distillation.　The percentage figures are based on the crude, and refer to volumes.　Stock C goes to a cracking still; B is re-run.　The paraffin distillate is merely air cooled; the next worm for the naphtha and water white is water cooled.

as that of the refluxed liquid.　When a number of cuts are drawn, their fractionation is not complete, and must be supplemented by a small column called the stripper, one for each cut, in which the cut is freed from all more volatile constituents than its set standard.　The "deck space" (distance between plates) should be sufficient to allow the vapor to disengage itself from the liquid; it varies from 10 to 24 inches.　The number of plates varies from 5 to 25, but averages 11 to 15 in stills for one overhead cut.　The vapor velocity is held at maximum; it is too high if it forces the liquor off the plates; 2 lineal feet per second is average, 3.5 is high.　A bubble tower handling 5500 barrels of crude per day, in one instance, is 92 feet high, and 6 feet in diameter; it is well lagged to preserve the heat.

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[12] Of the crude oil stills, 56 per cent are pipe stills (1936); the rest are presumably shell-type stills with batch operation.

Each plate has a number of small chimneys for the rising vapors, covered with bells or caps so that the vapor must bubble through the liquid on the plate. A downcomer carries the liquid to the next lower plate, and is sealed by its liquid. Baffles are placed across the deck so that the liquid must take a long path before it reaches the next downcomer. The capacity of a bubble tower depends upon its diameter and height, its efficiency upon the number of plates, the construction of caps, deck space, reflux procedure, velocity of vapors.

A tower unit would be called efficient if the gasoline fraction had an endpoint of 400° F. and the kerosene an initial boiling temperature of 400° F. An overlap of 25° F. would not be bad; an overlap of 50° F. would be poor efficiency.
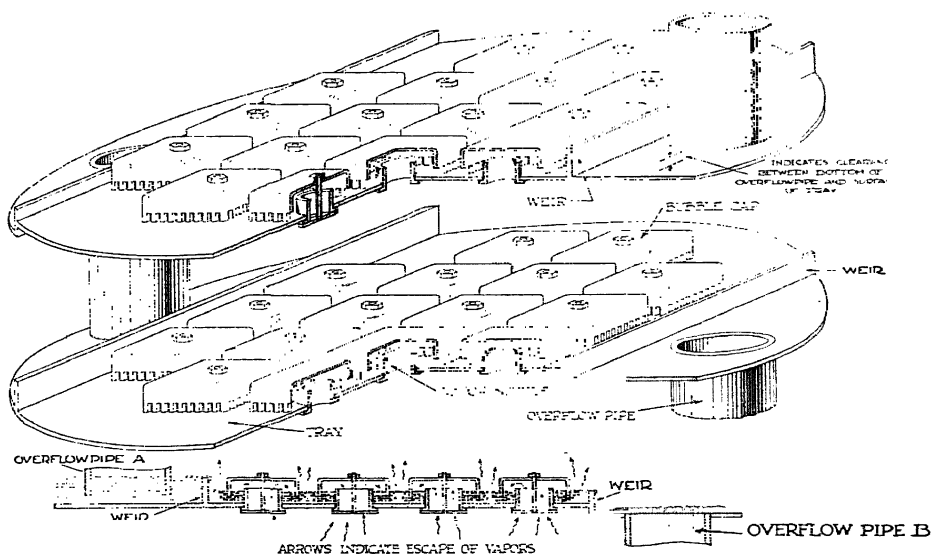
FIGURE 146.—Two plates in a bubble tower, showing the domes or bubble caps. the overflow or rundown pipes. and the weirs. (From the Petroleum Grade Crude Oil Association.)

Oil columns are operated at atmospheric pressure, at higher pressure, and with vacuum; the oil is distilled dry, or with a supply of steam to assist. When higher pressures are used, the temperature must be higher. The temperature at the base of the still must be such that the material is boiled.

Continuous Distillation-Skimming Unit. The new method of working is well illustrated by the diagrammatic flow sheet in Figure 147 of a 7000 barrels per day capacity unit of the Producers and Refiners Corporation [13] at Tulsa, Oklahoma. The crude oil picks up heat in the gasoline vapor heat exchangers, then, after passing through a settler for

[13] "One man operates new 7000 barrel pipe still skimming unit," Allen S. James, *Natl. Petroleum News*, **21**, 73, Nov. 27 (1929).

removal of any water, more heat in the crude oil heat exchangers. At a temperature of 350° F., it now enters the tubes of the furnace, where six oil burners raise its temperature to above 700° F., but below cracking temperature, for this is a skimming unit, that is, a plant for the separation of the gasoline and other fractions just as they are in the crude. The mixture of hot oil and vapors enters the bubble tower, and fractionation takes place. The tower is 10 feet in diameter, and 100 feet high. Gasoline vapors are taken off overhead, that is, at the top of the tower; a naphtha cut just below the top; next a kerosene cut; then a gas oil cut; while finally the residual oil forms the fuel oil cut at the bottom of the still. In conformance with the statements on fractionation, for so many cuts refluxing is necessary, and there is returned to the still a part of the gasoline, now cold, a part of the naphtha, and a part of the kerosene, both also cold. The effect of the return of such cooled liquids, to the point
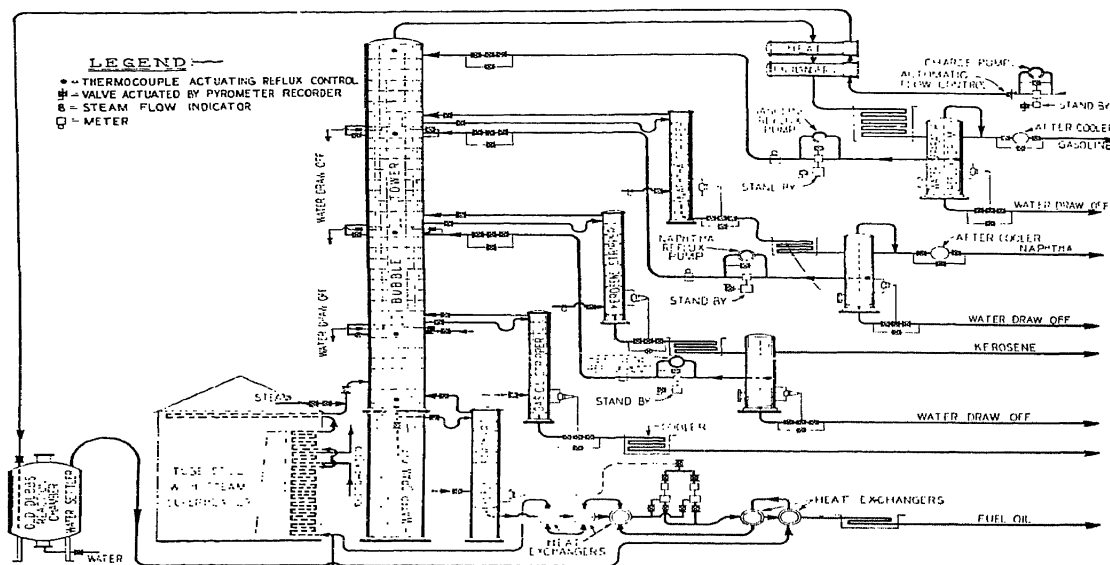
FIGURE 147.—Diagrammatic flow sheet for a 7000 barrel Tulsa unit, showing tube still, bubble tower, four auxiliary plate towers used as strippers, with condensers, after coolers, three reflux pumps, and heat exchangers. (Courtesy of National Petroleum News.)

in the still where material of similar composition is met by it, is essentially to retard the vaporization of the more volatile of the constituents. Each fraction is cleared of any admixed higher fraction in a small auxiliary plate tower, which receives superheated steam. (*See* Fig. 147.) For the kerosene, for example, the stripper returns overhead to the still a mixture of gasoline, naphtha and water vapors. Condensed water in the bubble tower is let out at the points indicated.

The fuel consumption, exclusively of the steam, is 1.5 per cent of the throughput. This unit replaces a battery of seven shell stills of the older type.

The chemical refining of the several products was done formerly by agitation with 66° Bé. sulfuric acid (generally 3 pounds of acid to each barrel of oil), followed by a water wash, then a dilute caustic soda wash.

FIGURE 148.—View of the tube still, in the 7000 barrel unit at Tulsa. The bubble tower can just be seen in the rear of the picture.
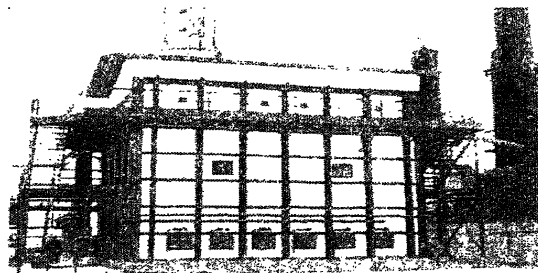
The amounts of sulfuric acid consumed are so great that methods for recovering it were developed; a plant for recovering the sulfuric acid from the "sludge acid" is part of many refineries. For sulfur-containing crudes the chemical treatment of the fractions includes an agitation with caustic soda saturated with litharge (PbO). Certain crudes require a special treatment with metallic oxides such as the one devised by Herman Frasch.[14]

There are now other methods for purification, for the purpose is no longer to remove all the unsaturated hydrocarbons, but only part of them. A gum-forming constituent may be recovered from the purification treatment and made the source of a valuable resin (Chapter 35). A modern method for purification which saves the by-products without injuring them is the Edeleanu process, which employs liquid sulfur dioxide. For this treatment, liquid sulfur dioxide is introduced near the top of a tower completely filled with the liquids; the well-cooled distillate (gasoline, naphtha, kerosene, or a lube fraction) near the bottom, both in spray form. The droplets of the distillate must rise through the body of the liquid sulfur dioxide; the droplets of the fresh solvent must sink through the layer of hydrocarbons. Two layers continue to form, the sulfur dioxide being the lower one (sp. gr. 1.45 at 68° F.); the hydrocarbons form the upper one. There is continual removal of the liquids to make room for the incoming material. The asphaltenes, carbogens and sulfur-containing impurities dissolve in the sulfur dioxide, and flow out with it. In a separate vessel, the sulfur dioxide is vaporized, re-compressed and re-cycled; there is left behind the extract, which may have a commercial value. The upper layer dissolves a small amount of sulfur dioxide; in a separate still, this is driven off by gentle heat, and saved; there is left the refined product.

[14] *Ind. Eng. Chem.*, **4,** 134 (1912).

Cylinder Stock and Wax Distillate.   Many crudes give distillates in the following order: light naphtha, heavy naphtha, water-white, gas oil, fuel oil, then wax distillate, which Figure 145 does not show, but is indicated in Figure 147, and the residuum, in certain cases the most valuable product.   The Pennsylvania grade crudes, which are always class A, leave a residue which is so low in suspended carbon and free from asphaltic impurities that it forms an article of commerce under the name of "cylinder stock."[15]   It is refined in a vacuum column still with steam injection, giving a "pressable wax distillate" overhead, and "600 steam refined" [that is, heated to 600° F. (315.5° C.)] as a bottom product, not volatilized; this latter is diluted with naphtha, filtered, chilled, and its suspended soft wax separated in a centrifuge, giving petrolatum.   The clear solution is passed through a still to drive off the naphtha, it may be bleached by passing it through granular clay, and there results "bright stock" with viscosity for example of 145 seconds at 210° F.

The wax distillate carries the hard wax.   It is chilled to 26° F. (−3.3° C.), and the suspension forced under a pressure of 300 pounds into a filter press set in a room which is kept cold.   The press may be, for example, 36 feet long, with 350 circular cast iron plates, 5 feet in diameter.   The filter cloth is cotton duck; the press has central feed.   Once a day the press is opened and the wax removed; as it still contains 40 per cent oil, it is "sweated," that is, warmed in shallow pans with false bottom on which the wax rests, while the oil flows into collecting troughs.   The wax left in the pans, now free from oil, is melted and run through bone char in cylinders 2 feet wide and 20 feet high, to remove the color The white wax is cast into blocks for shipment, or is made into candles.   In addition, it is used in laundries, for waxed papers and drinking cups, and for a variety of household purposes.[15a]

The oil filtrate from the wax press passes to a still, with steam injection, to give a gas oil, a non-viscous neutral oil, and as residue, the viscous neutral.   This latter is filtered through granular clay, and becomes the finished viscous neutral, with viscosity of 180 at 100° F.

Lubricating oils for the market are then produced by blending viscous neutral and bright stock in various proportions.

The value of cylinder stock is reflected in the price for Pennsylvania grade crude, which is double or even triple that for Oklahoma crude; thus, Pennsylvania grade in 1936 was $2.42 average; 1935, $2.17; 1933, $1.86; while Oklahoma crude was in the corresponding years $1.10; $1.00;

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[15] Example of cylinder stock:

Penn stock, viscosity	100–125	sec. at 210° F.
	1600	sec. at 100° F.
Coastal stock, viscosity	125–130	sec. at 210° F.
	3060	sec. at 100° F.

In early 1937, the quotations for cylinder stock in tank car lots ranged from 14½ to 18½ cents per gallon.

[15a] An interesting 29-page pamphlet on "Candle manufacture, with special reference to tropical climates," by Professor N. N. Godbole, has recently been published; it depicts the teaching of the making of candles in India, and the materials available, with their properties and costs.   Benares Hindu University, Benares, India, 1935.

and $0.62 per barrel. This higher value is one reason also that it is worth while in Pennsylvania to flood the oil sand with water in order to recover the residual crude.

The Dubbs Cracking Process

Several proposals have been made for a system which would allow the simultaneous distilling of the crude and the cracking of its heavier hydrocarbons, in an apparatus which would permit a continuous, or relatively continuous, operation. In the Dubbs process (Fig. 149), the pre-
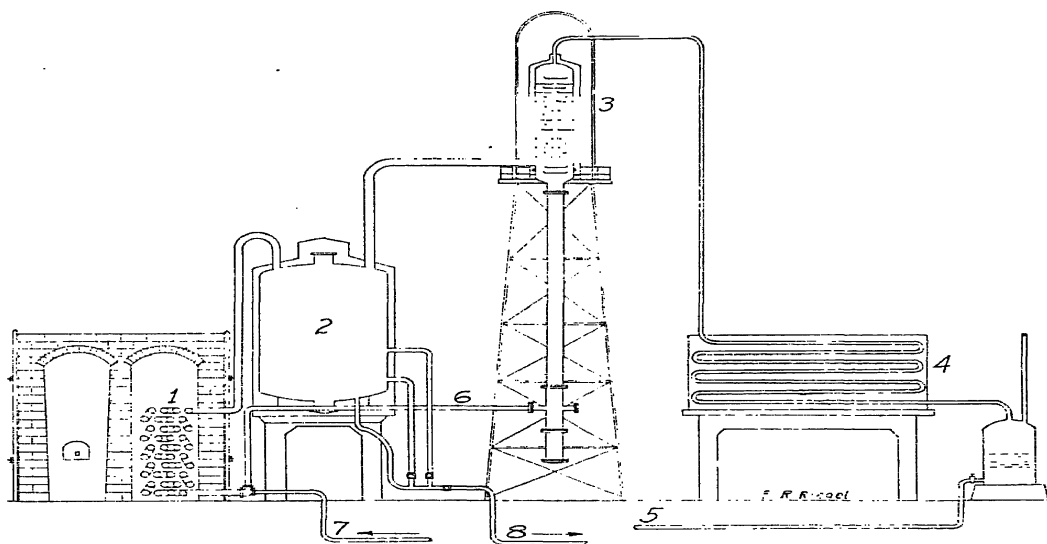
Figure 149.—Scheme for simultaneous distilling and cracking of crude oil (Dubbs patents). 1, heating coils; 2, vaporizing chamber; 3, dephlegmator, cooling coil not shown; 4, condenser for gasoline; 5, line from receiver to storage tank; 6, high-boiling parts of vapors condensed and returning to heating coils, joining fresh crude oil from 7. The operation is continuous. The use of 3 for topping crudes is given in the text.

heated crude oil (750° F. or 399° C.) is circulated through 4-inch steel tubes heated indirectly in a furnace to 840° F. (449° C.) under a pressure of 350 pounds. On leaving the heating coil the superheated oil enters a vaporizing chamber where it separates into gases and vapors which pass through a dephlegmator to a condenser; a liquid consisting of heavy portions which form the residuum; and a solid, coke, which accumulates in the bottom of the chamber. The dephlegmator reduces the temperature of the vapors so that only the gasoline fraction passes it; heavier hydrocarbons are condensed and drop into a reflux leg from which they are returned with fresh oil to the heating coils. The dephlegmator has a cooling coil in which the fresh oil circulates; by varying the quantity of cold oil sent in, the temperature is controlled; it is in this coil that the fresh oil is preheated. The action in the dephlegmator is controlled fur-

ther by the spraying of oil directly into the vapors; fresh oil is used, and its temperature is raised sufficiently so that such gasoline as it contains is vaporized and passes to the condenser with the uncondensed vapors from the chamber. Such fresh oil which is made to give up its gasoline is called "topped oil"; the remainder of such oil also drops in the reflux leg and from there is pumped through the heating coils.

The functioning of the system is controlled by the pressure under which it operates, and this is determined by the position of a needle valve, the release valve, set at the receiver for the condensed vapors which leave the cold-water condenser. The liquid in the distillate receiver is treated with chemicals if necessary, to produce the purified gasoline.

The Dubbs process [16] provides admirably for the handling of such crudes as contain no lubricating oil fraction; for they are made to yield an increased amount of gasoline; the other products are fuel oil from the residuum, by merely cooling it, and coke. The operation is limited as to continuity by the capacity of the vaporizing chamber for coke, and the amount of coke deposited will vary with the kind of crude used; by building two chambers, this limitation is removed. There remains in that case the fouling of the heating tubes by the coke which accumulates there; a period of 11 days is considered fairly good. In order to lengthen this period, the system must be fed not with crude oil, but with a fraction obtained in the course of a previous distillation in a bubble tower. This procedure has become the general practice, and the fraction is called cracking stock. In general, for every barrel of gasoline, there is formed a barrel of "heavy residue" (*see* under bunker oil).

Other important processes [17] which crack by heat and pressure are the Cross, the Holmes-Manley, and the Ellis. In the Cross process, as in the Dubbs, the oil is passed through a coil laid in a furnace, and then delivered into a horizontal vaporizing chamber which receives no outside heat; the operating pressure is higher than in the Dubbs, namely 600 pounds. The Cross process has been very successful. In the Holmes-Manley, the oil is heated in stills 3 feet in diameter and 40-feet high, provided with stirrers, at a pressure of 175 pounds. The Ellis is a tube and tank system.[18]

THE DE FLOREZ PROCESS FOR CRACKING CRUDE OIL DIRECTLY

As a rule, when crude oil is fed directly into the tube still of a cracking unit, the latter are fouled by coke; the vaporizing chamber also collects coke. In the De Florez process,[19] a way has been found to handle

[16] *Chem. Met. Eng.*, **31**, 1006 (1924) and U. S. Patents 1,123,502, 1,231,509 1,135,506, 1,319,053.

[17] Descriptions and sketches will be found in *Chem. Met. Eng.*, **31**, 812, 849, (1924).

[18] There are 33 different processes for cracking. 57 installations are the plant's "Own," with 520,000-barrel capacity per day; 55 are Dubbs with 387,400 barrels; 22 are tube and tank, with 443,000 barrels; 41 are Cross, with 200,600 barrels; 19 Holmes-Manley, with 186,500 barrels; 9 De Florez, with 32,000 barrels; 10 Donelly with 35,000 barrels capacity per day. There were 8 combination units which skim the crude and at the same crack the heavier molecules, with a crude oil capacity of 95,000 barrels a day. From "Petroleum refineries including cracking plants in the United States on Jan. 1st, 1936," R. G. Hopkins and E. W. Cochrane, *U. S. Bureau of Mines, I. C.* 6906.

[19] "Control of gasoline and fuel oil quality in cokeless cracking process," Paul Truesdell, *Natl. Petroleum News*, **21**, 69, part 2, May 1, (1929).

crudes so that there will be no coke formation. The apparatus consists of the parts shown in Figure 150, including heat exchanger, bubble tower, reflux cooler, pumps, and a circular, vertical pipe still. In the standard set, the pipes are 42-feet tall, of special steel, and number 102. They are set in two concentric circles, and so spaced that the rear ones receive radiations as fully as the front ones. The operation is as follows:

The crude oil is preheated in the heat exchanger and injected into the bubble tower just above the inlet of the heated oil from the still. Its gasoline is distilled off (skimmed), while the heavy ends pass out of the bottom of the tower, neither of these fractions having reached the heater at all. A gas oil stream is bled off at point *A*, and after passing through the accumulator *J*, enters the pipe still, whose tubes are equidistant from the flame in the center and heated by radiant heat only; the flame does

Figure 150.—Flow sheet for the De Florez process for cracking oil for gasoline without coke formation. *A*, gas oil line to storage tank *J*; *K*, pump to circular furnace *D*. *C*. hot crude oil entry to tower. *M*. return of part of the gasoline.
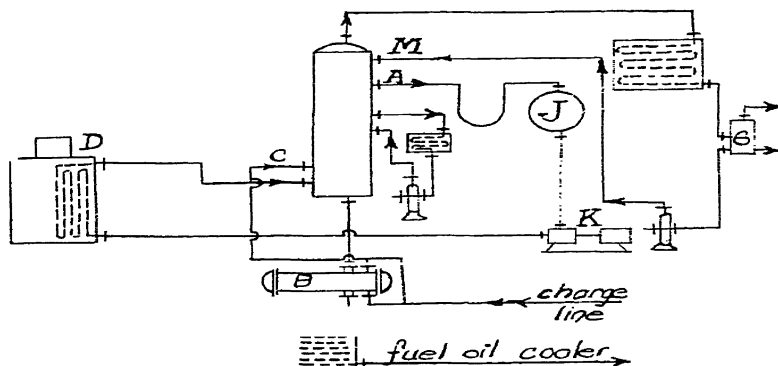
not impinge upon the tubes. The superheated oil enters the bubble tower, where its newly formed volatile constituents separate and later pass out at the top. Unchanged material gets back into the gas oil stream and is recirculated through the heater. Thus only clean stock reaches the tubes in the still.

A portion of the charge in the tower is drawn off below point *A* and cooled, then fed back into the tower by a pump. The purpose is to control the fractionation, chiefly by retarding the volatilization of naphtha.

It should be noted that in this case the bubble tower functions both as expansion chamber and as fractionating column.

The pressure at which the bubble tower is operated is the factor governing the nature of the products. With the pressure in the tower 80 pounds, at the still just before entering the furnace 330 pounds, and the temperature at that same point 1000° to 1100° F. (531° to 590° C.), a Venezuela crude (4.5 to 8 per cent gasoline) gave as products: 30 per cent gasoline, 63 per cent fuel oil, and 7 per cent fixed gases. The gasoline produced boiled between 100° and 384° F. (38° to 196° C.).

With lower pressure, for example 20 pounds, the gasoline yield is smaller, the fuel oil fraction greater. Increasing the temperature and

pressure on the bubble tower raises the antiknock value of the gasoline, but at the same time raises also the absolute quantity of fixed gas.

With a pressure of 100 pounds in the furnace the De Florez is a vapor phase cracking unit; with 400 pounds, it is a liquid phase cracking system.

For the *purification* of the cracked gasoline by any method the standard sulfuric acid process is used, or the Edeleanu liquid sulfur dioxide proc-
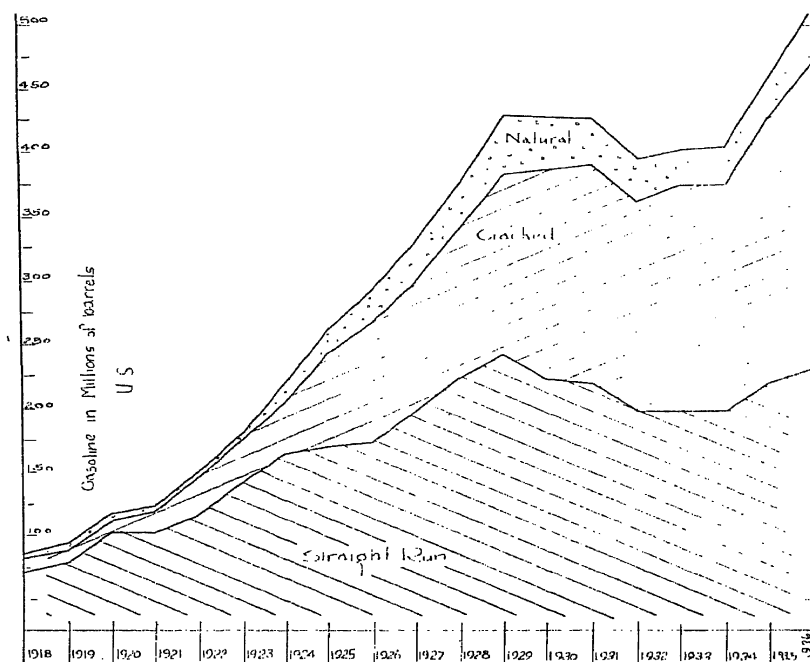
FIGURE 150a. — Curves showing the yearly amounts of straight, cracked, and natural gasoline which, with b e n z o l (not included), make up the motor fuel figure in the United States, based on graph in *Oil and Gas Journal,* (May 21, 1935), extended.

ess; other special processes such as the Halloran, in which the gasoline is treated with much acid in 3 steps, at low temperatures (0° F. [—17.8° C.]), and the Lachman process, in which the hot hydrocarbon vapor meets a concentrated zinc chloride solution,[20] have met with success.

Preceding the purification, it is customary to stabilize the cracked gasoline produced, which means in this case driving out its dissolved propane and butane gases by heat.

In the McAfee process, 5 to 8 per cent anhydrous aluminum chloride is heated with an absolutely dry oil fraction, at atmospheric pressure, with stirring. The temperature is 550° F. (288° C.), and the period 48 hours. An excellent quality of gasoline is obtained, which requires only a wash with dilute alkali. The success of the process depends upon a cheap enough supply of aluminum chloride. For this purpose a remarkable process has been developed, in which bauxite and carbon

[20] *Chem. Met. Eng.*, **42,** 414 (1935).

mixed are projected by a jet of chlorine containing oxygen and nitrogen into a chamber held at the proper temperature. The chloride forms granules which drop out of the way of the incoming materials.[21]

The average gasoline yield by cracking is at best 60 per cent on the cracking stock; by combining hydrogenation with pressure cracking, the yield may be increased to 108 per cent. The reduction of available crude will favor the adoption on the large scale of this combination process.[22]

The relative importance of straight run gasoline, cracked gasoline and other motor fuels is shown in Table 47:

TABLE 47.—*United States Production of Motor Fuel (in Barrels of 42 U. S. Gallons). Showing Gasoline Production by Different Methods.**

	in thousands of barrels		
	1936	1935	1934
Straight run gasoline	231.287	219,583	206.337
Cracked gasoline	239,620	207,537	182.433
Natural gasoline	42,041	39.333**	36.556
Benzol	2,537	1,871	1,708
Total motor fuel, U. S.	515,485	468.021	423.801

* Bureau of Mines.

** Of this total 3.223,000 barrels were exported, while 2.833.000 barrels were lost: 30,280.000 barrels were used at the refineries, for blending; the balance was blended by dealers or sold as such.
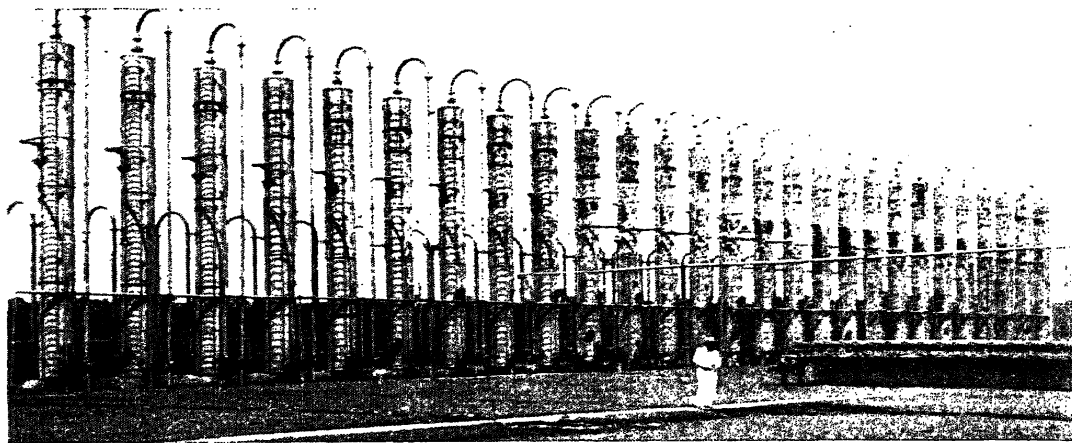
FIGURE 151.—A natural gasoline extraction plant; the wet gas passes through the 27 towers in succession, entering at number 1, leaving at number 27. The fresh oil enters at 27, and travels toward 1. Monroe field, Louisiana. (From the National Geographic Magazine.)

Natural gasoline is the liquid which accompanies the "wet" natural gas in many regions; it is removed by passing the gas through a large number of straw oil towers. After the oil is saturated, it is heated

[21] "Cheap aluminum chloride," A. M. McAfee, *Chem. Met. Eng.*, **36**, 422 (1929), or U. S. Patent 1,867,672.

[22] *Bull. Am. Ass. Petr. Geol.*, **20**, 43 (1936).

gently, the gasoline collected, and the oil, after cooling, used over again. Activated charcoal, silica gel, and activated alumina, as well as other absorbing agents, are also in successful use, replacing the straw oil.[23]

Petroleum Coke, Bunker Oil.   In the old batch operation with shell stills, an accumulation of coke took place gradually, so that every seventh day, the still had to be cleaned out by removing with picks and bars the coke which had formed.   There is no counterpart to-day for the batch still where the coke might accumulate; it is not allowed to develop into deposits anywhere, but is swept along with the crude through the pipe still, carried into the bubble tower, and discharged with the residuum; this latter may carry asphaltic matter besides.   Much of such residuum forms the fuel in the refinery.   Some of it is sold for fuel for steam boilers, at perhaps 3 cents a gallon under the name bunker oil.[24]

Another source of bunker oil is the heavy residue from the cracking process, with perhaps a small addition of gas oil to make it more fluid.

A process to "stabilize" bunker oil, so that it will not develop sediments in transit and in storage, is the Goodwin process, which consists of "chemical and mechanical treatment of the residuum leading to two materials of value, a stabilized fuel oil, merchantable as Bunker A, B, and C, and a high Btu. value residuum suitable as a refinery fuel or a briquette binder."[25]

The demand for coke in the meantime has become insistent; to meet it, some of the residuum is run into a batch still and distilled to dryness.   A certain amount of fuel oil is collected, and the coke is allowed to deposit. It is later removed as in the old days, and sold for 6 to 7 cents a pound for making electrodes.   Petroleum coke is ash-free.

HYDROFINING: THE HIGH PRESSURE CATALYTIC HYDROGENATION OF PETROLEUM FRACTIONS

A recent development in petroleum refining is the hydrogenation of low-grade fractions, to produce high grade standard products, or new products with superior qualities.   It is the result of the combined effort of the German I.G. (Interesse Gemeinschaft der Farbenindustrie) and the Standard Oil Company of New Jersey.   The process permits the production of a lubricating oil possessing all the desirable properties for such an oil, a result never before attained.   Another adaptation is the conversion of heavy crudes and refinery residues into gasoline low in sulfur, without the formation of coke.   Still another is the transformation of poor quality gas oils into hydrogenated gasolines with high anti-knock properties.   While the present cracking methods allow the up-

[23] "The recovery of gasoline from natural gas," George A. Burrell, Chemical Catalog Co., Inc., N. Y., 1925.

[24] Two samples of bunker oil .

	Sample 1	Sample 2
A. P. I. gravity	15.9	19.9
Saybolt viscosity at 100° F.	207	155
Flash (open cup)	225° F.	200° F.
A. S. T. M. Pour (max. for 115° F.)	50	45
A. S. T. M. Pour (min. for 220° F.)	–10	–20

[25] Dr. T. R. Goodwin, *Nat. Petroleum News*, 21, (2) (May 15, 1929).

grading of a part of the stock charged, the remainder is degraded into tars and coke; with hydrogenation, however, it is feasible to upgrade all of the stock charged, and transform it into the more valuable, lower boiling distillates.

The lubricating fraction to be treated, either paraffin base, naphthenic base, or mixed, is pumped under a pressure of 3500 pounds per square inch, with hydrogen gas under the same pressure, through a heat exchanger, then through gas-fired heating coils, at a temperature of 800° F. (427° C.) to four reaction chambers, which contain the sulfur-resistant catalyst. The reaction chambers are 40 feet high, 3-inch internal diameter, forged from nickel steel, with wall 7 inches thick. The catalyst is molybdenum oxide deposited on alumina shaped into 1-inch cubes. In these chambers the molecule is rearranged into its most stable form (stabilization), combined with hydrogen, while at the same time the elements oxygen, nitrogen, and sulfur form their relative hydrides, leaving the oil molecule (purification). Another change is the production of a more homogeneous mixture of molecules than contained in the entering stock, by preferential rearrangements of the more complex molecules (homogenization). The reaction requires but a very short time, and is exothermic.

The mixture of oil and gases passes through the exchanger, and is cooled, reaching a separator where the gases pass off, still under a high pressure. The unused hydrogen may be recovered by scrubbing out (oil) the hydrogen sulfide and other hydrides, and returned to the entering charge. The hydrogen sulfide may be recovered and by burning it with a limited supply of air, its sulfur recovered as such.

The liquid from the separator is then fed to a fractionating column, and separated into gasoline, gas oils, and the residue. This latter is divided into several fractions (cuts), dewaxed, and subjected to minor treatments, when they are ready for the market. No coke is formed during the operation.

The lubricant obtained has the five qualities required in a perfect lubricating oil: (1) High viscosity index, (2) low pour point, (3) resistance to oxidation, (4) negligible carbon formation, (5) long life. To this may be compared the paraffin base lubricating oil, which possesses qualities (1), (3), and (5), and naphthenic base lubricating oils, which possess (2) and (4). By pour point is meant the temperature just below which the oil is too thick to pour.

Viscosity Index. To give the viscosity index [26] of an oil is a way of evaluating it with respect to its viscosity-temperature behavior, and it is a way which has become universal. Any oil becomes less viscous as its temperature is raised. A high viscosity index means that this decrease is moderate, no more than should be expected. A low viscosity index means that an oil thins rapidly, so that at elevated temperatures it is like water, and of no value as a lubricant. The temperature index chart (Figure 152)

[26] "Viscosity variations of oils with temperature," E. W. Dean and G. H. B. Davis, *Chem. Met. Eng.*, 36, 618 (1929); "Alignment chart for estimation of viscosity index of oils," I. Laird Newell, *Ind. Eng. Chem.*, 23, 843 (1931).
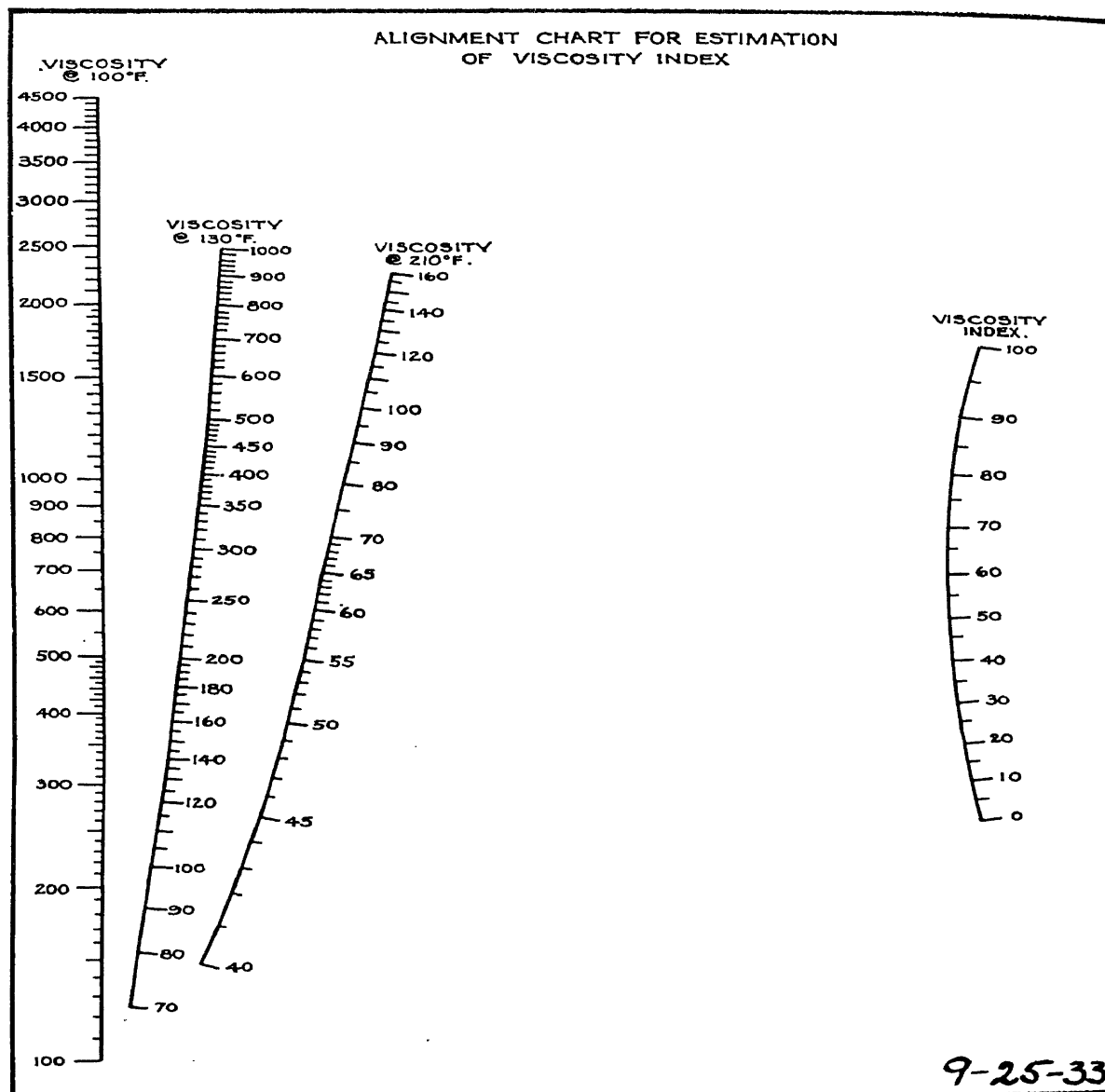
FIGURE 152.—Viscosity chart for estimating the viscosity index of a lubricating or other oil, based on the tables of Dean and Davis, *Chem. Met. Eng.*, **36**, 618 (1929), corrected for the low viscosities. (Kindly supplied by Dr. E. W. Dean, Standard Oil Development Company.) In order to use chart, find viscosity in Saybold seconds, at 100° F. (37.8° C.), then for the same sample, at 210° F. (98.9° C.); lay a straight edge to connect the two points on the proper curves, and read the numeral under viscosity index. This chart is only slightly different from the one p. **43**, *Ind. Eng. Chem.*, **23**, (1931) (I. Laird Newell).

is based on measurements on two series of oils,[27] and on two mathematical expressions.

Vapor Phase Hydrogenation. The hydrogenation of a lubricating oil fraction is a liquid phase reaction. When gas oil is hydrogenated completely to give gasoline, the reaction takes place in the vapor phase. Hydrogenated gasoline has a high flash point, so that it is less susceptible to explosion than ordinary gasoline. This is "safety gasoline." It is very sensitive to the addition of tetraethyl lead, so that a smaller percentage added will reduce knocking as much as five-fold in certain of the ordinary cracked gasolines.[28]

FIGURE 153.—A vacuum distillation tower, which receives the lubricating stock and separates it into several "cuts," preparatory to propane and solvent refining; with its three stripping vessels at its base. (Union Oil Bulletin, Nov., 1934.)
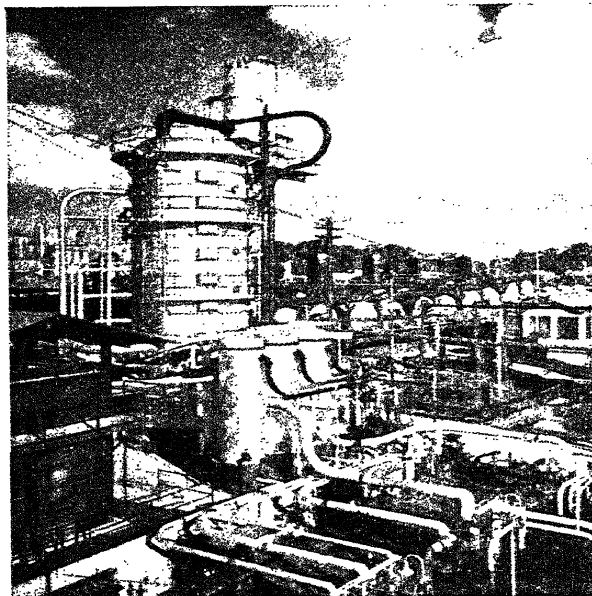
Solvent Purification of Lube Fractions. The purpose of the several processes known as solvent purification processes has been the production of an acceptable or superior lubricating oil from an inferior lube fraction. The process might involve the precipitation of the undesirable portion, or the extraction and removal of the desirable portions, or both. These processes have gained a well-merited, wide publicity. For illustration, the process employed in California will be sketched.[29]

Certain western lubricating fractions contain several classes of hydrocarbons: Asphaltenes, high melting thermoplastic solids, low in hydrogen, high in carbon, very undesirable. Carbogens, a transition class from

[27] Series of oils H, moderate decrease in viscosity on heating; series L, considerable decrease.
[28] Further data will be found in "Hydrogenation of petroleum," R. T. Haslam and R. P. Russell, *Ind. Chem.*, 22, 1030 (1930).
[29] *Union Oil Bulletin*, November, 1934, containing "Research behind Triton," Ulrich B. Bray; and "From test tube to reality," Earle W. Gard.

asphaltenes to viscous oils, low in hydrogen, high in carbon, undesirable naphthenes, cyclic compounds of the polymethylene series, more stable than the carbogens, but under severe conditions, sludge forming, undesirable. Parathenes, consisting of naphthene rings with paraffin side chains, the highest type lubricating oil hydrocarbons. Paraffins, which resemble parathenes, but with the paraffin side chain predominating, so that at room temperatures the higher members are solids, called petrolatum if soft, waxes if hard. On comparing this list with the table for the classification of crudes, it will be seen that there is no conflict.

FIGURE 154.—At the far left, two propane storage drums; the three vessels in center are part of the de-asphalting plant; at the right, the propane and oil recovery columns. (Union Oil Bulletin, Nov., 1934.)

A selection of wax-bearing, naphthenic crudes is made, and distilled in the bubble tower, to give among others a wax distillate fraction. This fraction is again distilled in a plate tower under a high vacuum, giving several cuts, which are then treated separately. The agents are liquid propane, low temperatures, liquid sulfur dioxide, or a liquid sulfur dioxide-benzene mixture (with 25 per cent benzene). Several volumes of liquid propane (a reagent at the ready command of almost any refinery) are mixed with one volume of the lubricating oil fraction; the asphaltic fraction separates, and collects as a lower layer, while the propane dissolves the good oil, and the wax.

The propane oil layer passes to chilling vessels, where by lowering the pressure, a part of the propane volatilizes, thus reducing the temperature to −40° F. (−40° C.); wax separates. The solution receives fresh liquid propane in order to maintain the original ratio. The chilled suspension is kept circulating to prevent the settling out of the wax, which is finally removed by filtration of the chilled material. The clear oil-propane passes to propane recovery towers, where the propane is removed by distillation. The residual oil now passes to the solvent treating plant where it meets a sulfur dioxide-benzene mixture which removes the carbogens and most of the naphthenes. Two layers form, with the sulfur dioxide solution of the carbogens and naphthenes the lower one. The parathenes, considered the highest type of hydrocarbons for lubricating

purposes, and the paraffins, form the upper layer, which is passed through a still to remove the small amount of sulfur dioxide it contains, then bleached by means of granular clay, and is then ready for the market. Such an oil is held to have all the qualities which a good lubricating oil should have, and no defects. In the course of the purification, about half the original fraction is rejected.

In the Duo-Sol process,[30] two solvents operate in a series of 9 pressure vessels and travel in opposite directions. At 9, propane, one of the solvents, loaded with paraffins and parathenes, leaves the system to deliver the purified lubricant; fresh cresylic acid (63 per cent cresylic acid with 37 per cent primary phenol), the second solvent, enters at 9 and travels to 8, 7, until it reaches 1 where it leaves, laden with asphaltenes and carbogens. The fraction to be treated (thus a 23° A. P. I. residual oil from an Oklahoma crude) enters at 3. Fresh propane enters at 1. The liquids are moved from one division to the next by means of small, high speed centrifugal pumps.

Still another process employs "Chlorex," β-β'-dichlorethyl ether. $CH_2Cl.CH_2.O.CH_2.CH_2Cl$.[31]

Antiknock Compounds. In order to prevent the familiar knock in an internal combustion motor such as in automobiles, and the loss of power which occurs simultaneously, a number of substances may be added to the fuel with success. The effectiveness per unit weight of these substances varies greatly. The best known antiknock compound is tetraethyl lead, $Pb(C_2H_5)_4$, a liquid which is also the most efficient, for 0.04 per cent of tetraethyl lead will retard the detonation as much as does 25 per cent of benzene.[31a] Tetraethyl lead is made by the action of ethyl chloride on a lead-sodium alloy of definite composition, in the presence of a small amount of ethylene bromide.

The antiknock compound is a mixture of 3 parts by volume of tetraethyl lead, a liquid, with 2 parts ethylene bromide; this mixture is added to the gasoline, with a small amount of bromonaphthalene, and a red dye (*see* Chapter 28), and the treated gasoline is then retailed. The ethylene bromide is added in order to change the lead oxide formed during the combustion to the volatile lead bromide which passes out with the exhaust gases. The use of gasoline containing tetraethyl lead allows the use of high-compression motors and thus increases the power efficiency of the fuel.

The general use of tetraethyl lead in gasoline was delayed because of the fear that it might prove poisonous, harmful to health; there is no reason for this fear.[32]

There are many other substances which have antiknock properties, among others aromatic hydrocarbons such as benzene, and the unsat-

[30] *Compare* "Refining lubricating oils by solvent extraction," J. V. Hightower, *Chem. Met. Eng.*, **42**, 82 (1935); and "The Duo-Sol process," Max B. Miller, *Ibid*, 285.
[31] "A review of the commercial applications of 'Chlorex,'" by W. H. Bahlke, A. B. Brown, F. F. Diwoky, *Oil and Gas J.*, **32**, Nos. 3, 60, 62, 72 (1933).
[31a] *Ind. Eng. Chem.*, **14**, 894 (1922).
[32] *Public Health Bull.* **No. 148**, Washington, D. C., 1925.

urated open chain compounds such as the olefins so that cracked gasoline has long since been accepted as superior to the straight-run gasoline from class A and B crudes.

The methods of washing the distillate are being modified with the same end in view; the tendency is to do away with the strong sulfuric acid wash and to substitute dilute acids or a different process, as, for example, the purification in the vapor phase by fuller's earth.[33] The removal of the unsaturated hydrocarbons is largely prevented by the newer methods of washing.[34]

Iron carbonyl is used to some extent in Europe as an antiknock compound; it has not come into use in America, for it requires frequent cleaning of the spark plugs due to the formation of magnetic oxide in the gap.

There is at the present time no satisfactory theory for the action of an antiknock agent, such as tetraethyl lead. One of the most reasonable, but still unestablished, is that the lead compound absorbs certain heat radiations and thus prevents premature combustion.[35]

Octane Number. The octane number is the rating of a gasoline as to its antiknock properties on the basis of a standard sample consisting of "iso-octane" and normal heptane mixed in various proportions. The older standard was a benzene addition. Normal heptane tends to knock, while "iso-octane", which stands for 2-2-4-trimethylpentane, has marked antiknock tendencies, so that by mixing the two in all proportions, a series of fuels are obtained which cover the whole scale of possible gasoline mixtures; such a series is exact, and reproducible. It is used as primary standard; selected gasolines are compared to them and then serve as working standards, because they are cheaper. A gasoline has octane number 70 if on compressing it in a standard engine, it begins to knock with the same compression ratio which causes a mixture of 70 parts "iso-octane" and 30 parts *n*-heptane, to develop a knock in the same engine under the same conditions.

The density and boiling points of "iso-octane" and *n*-heptane are almost identical, an advantage for this purpose.

High Octane Fuel. In order to develop maximum power from a given weight of fuel, a high compression ratio must be used, and this in turn calls for a high octane fuel. As a consequence, aviation has been interested in the production of a 100-octane product, which is pure iso-octane, and which is now produced on the semi-commercial scale. It is made by polymerizing iso-butylene, isolated from refinery gases, into di-isobutylene by the action of sulfuric acid, at 90° C. (194° F.), and hydrogenating this unsaturated compound to iso-octane. There is in the laboratory stages a still higher octane fuel, the "iso-decane."

[33] The Gray process, U. S. Patent 1,340,889; described also in *Chem. Met. Eng.*, **31**, 975 (1924), by D. M. Liddell.

[34] "Refining of gasoline and kerosene by hypochlorites," Dunstan and Brookes, *Ind. Eng. Chem.*, **14**, 1112 (1922).

[35] *Compare* article by Graham Edgar in "The Nucleus," published by the Northeastern, Conn., and Rhode Island sections, American Chemical Society, February, 1927, p. 17.

It has been shown also that adding iso-propyl ether to the regular gasoline permits the production of 100-octane products.[36] and it is expected that this mixture will be welcomed by many interests.

Polymer Gasoline. The polymerization of olefin-bearing gases has as its main object the production of high octane motor fuel.[37] An almost ideal charging stock is the gas formed in a vapor phase cracking process. The apparatus resembles the cracking plant. The gas enters a furnace pipe coil, to bring it to the reacting temperature, then passes into the reaction coil, somewhat cooler, in which the polymerization takes place. Next follows the "arrestor", a small vessel in which a stream of cold oil meets the vapors and chills them, in order to stop the action; otherwise an undue amount of tars might be formed. The remainder of the process consists of separating the unchanged or newly-produced gases from the liquids; the latter are redistilled, and the gasoline fraction stabilized. The temperature of the furnace coil is 900 to 1000° F. (482 to 538° C.), and the charging gas is compressed to 600 to 800 lbs. pressure (termed low-temperature—high-pressure polymerization). It is estimated that the 90 vapor phase cracking plants in the United States produce 100 million cubic feet of gas daily, from which there may be produced 2,730,000 barrels of 78-octane gasoline per year, with much gas left over, and other products.

It is estimated that the liquid phase cracking stills produce 1,000 millions cubic feet of gas per day, from which there may be produced 30 million barrels of 100-octane gasoline per year. In this case the heating and reaction coils should be at 1,150 to 1,300° F. (621 to 704° C.), and the pressure on the charging stock 50 to 75 lbs. per sq. in.; this would be termed high-temperature—low-pressure polymerization. The gasoline produced contains from 80 to 85 per cent aromatics, that is benzene, toluene and the like.

In the computation of prices, if the charging stock is given a value approximating that for heavy fuel oil, since it otherwise possesses only its heating value, polymer gasoline can be produced for 5 cents per gallon.

As to natural gas, the washed gas from a natural gasoline absorption system for example, containing no unsaturated hydrocarbons, would pass a pyrolysis coil in which unsaturated hydrocarbons (and hydrogen) would form, then a reaction coil, the arrestor, and the separation and condensation apparatus. The natural gas produced in 1933 was 1,555,474,000,000 cubic feet, from which there can be made 77,800,000 barrels of 104-octane gasoline per year. The polymer gasoline from these various sources would be not far from 20 per cent of the 1936 regular gasoline production. From 1000 cubic feet of gas there will be produced 2.4 to 4.4 gallons of high test gasoline; by passing the residual gas through a second or third time, some more gasoline will be obtained. It may be worth while to indicate that the gas after the third pass will contain 40 per cent hydrogen, and

[36] The Standard Oil Development Company, New York.
[37] Taken in large part from "The thermal process for polymerizing olefin-bearing gases," M. B. Cooke, H. R. Swanson, and C. R. Wagner, *Petrol. Inst., Los Angeles meeting* (1935).

therefore it invites consideration as a source of hydrogen for synthetic ammonia.

There are several plants in operation at the present time (1937).

Processes using solid catalysts have also been developed. In one of these, the catalyst is solid-phosphoric-acid, and the gases are heated to about 450° F. (232° C.) under a pressure of 200 lbs.[38]

Butane is a gas at 26° F. (−3.3° C.) and atmospheric pressure; it has been produced in large quantities and may be shipped liquefied by tank car, by truck, and by pipe line from East Texas to the Gulf, and from Texas to St. Louis, Mo.; in 1935, its sales were estimated at 34,240,000 gallons, for domestic gas and enrichment of artificial gas, and in large additional amounts for polymerization. Five polymerization plants were expected to each use 1 million gallons of butane (liquefied) per day in 1936.[39]

TABLE 48.—*Charging Stock for Polymerizing Plants, for the Production of High Octane Gasolines.** (In Moles Per Cent)

	Gyro vapor-phase gas (2 samples)		Stabilizer overhead discharge (2 samples)		Natural gas d1	Same natural gas after pyrolysis d2
CH₄ + H₂	32.5	37.9	0.5	1.2	70.5	H₂ = 11.5 / CH₄ = 62.5
C₂H₄	23.9	25.6	9.2	7.1		15.7
C₂H₆	13.4	13.8	8.3	7.8	12.7	5.1
C₃H₆	16.8	16.8	40.3	37.6		2.5
C₃H₈	4.9	3.1	10.4	11.6	10.3	1.2
C₄H₈	6.1 } 2.8		28.4	30.5		1.5
C₄H₁₀ and up	2.4 }		2.6	3.4	6.5	0.59
Spec. grav. (air = 1)	1.035	.95			.645	

(1 cu. ft. of d1 besides producing gasoline, left behind 0.91 cu. ft. of new gas d2.)

* "The thermal process for polymerizing olefin-bearing gases," M. B. Cooke, H. R. Swanson, and C. R. Wagner, Sixteenth Annual Meeting, Los Angeles, American Petroleum Institute, 1935.

Cetane Rating. For Diesel oils, a system of rating analogous to the octane rating for gasoline has been established. The best Diesel fuel is the straight-chain paraffin, normal cetane, $C_{16}H_{34}$; the worst is α-methyl naphthalene, just the opposite from the gasoline fuels. Mixtures of these two substances serve as standards, and the cetane number is the percentage of cetane in a mixture with α-methyl naphthalene which gives the same ignition performance (measured in direct ignition lag) as the fuel tested. For heavy fuels, a cetane number of 30 gives a good performance, while for the lighter Diesel engines, a lighter fuel testing 40 to 60 cetane is chosen.[40] The best Diesel fuel comes from a gas oil cut from a class A or B crude.

Petroleum as a Raw Material for Alcohols. The cracking of heavy hydrocarbons may be so directed that the unsaturated hydrocarbons of low molecular weight, such as ethylene, C_2H_4, propylene, C_3H_6, and butylene, C_4H_8, may be produced; these may be dissolved in sulfuric acid

[38] "Polymer gasoline," Gustav Egloff, *Ind. Eng. Chem.*, **28**, 1461 (1936).
[39] *Oil and Gas J.*, **34**, No. 34, (Jan. 0, 1936).
[40] Specification for Diesel oil will be found in the Appendix.

and the acid esters so formed may then be hydrolyzed, giving the corresponding ethyl, propyl, or butyl alcohols, as well as others. Both the gases and the sulfuric acid are cooled, and the absorption may be performed under pressure in a series of absorbers which allow at the same time a separation. The temperature may be $-20°$ to $0°$ C.; a low temperature is sought because polymerization into larger molecules is thus prevented. The saturated sulfuric acid liquors are diluted by 3 volumes of water, an undissolved upper layer removed, and the acid liquor heated in a lead-lined steel still; the alcohols distill over. Example:

$$CH_3 . CH : CH_2 + H_2SO_4 \rightarrow CH_3 . CH(SO_4H) . CH_3$$
propylene   *ester*

$$CH_3 . CH(SO_4H) . CH_3 + H_2O \longrightarrow CH_3 . CH(OH) . CH_3 + H_2SO_4$$
          isopropyl alcohol
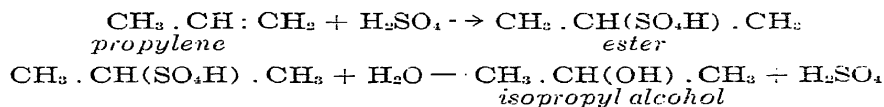
It is interesting to note that the water molecule which enters the olefin distributes itself in such a way that the hydroxyl ion becomes attached to the carbon having the least hydrogen. As a result secondary and tertiary alcohols form, and no primary, except in the case of ethylene.

Instead of hydrolyzing, chlorination may be performed and a different series of products obtained, such as dichloroethylene. Regarding the use of a pentane fraction, see Chapter 20.
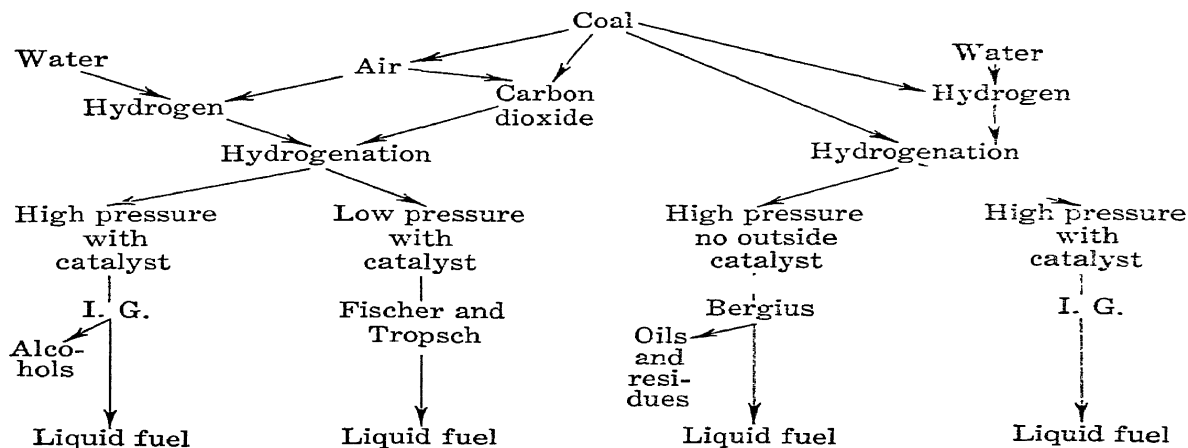
Tabular view of processes for the liquefaction of coal by hydrogenation.

OTHER SOURCES OF MOTOR SPIRITS

When the supply of crude oil gives out, the chemical engineer will turn to one or more of the other sources of motor spirits which have been developed in the recent past.[41] Motor benzene from the high temperature distillation of coal has been discussed in Chapter 14. The complete liquefaction of coal by hydrogenation at rather low tempera-

[41] "Future trends in automotive fuels," A. C. Fieldner and R. L. Brown, *Ind. Eng. Chem.*, **18,** 1009 (1926).

tures and high pressure, the method of Bergius, will yield about 40 gallons of motor spirits per ton, besides 50 gallons of Diesel oil, 35 gallons of fuel oil, and 10,000 cubic feet of gas. In this process [42] the powdered coal is mixed with oil from a previous run to a thick paste and heated to 400° C. (752° F.) in an atmosphere of hydrogen under the pressure of 150 atmospheres. In the I.G. process, the coal is hydrogenated in the presence of catalysts.
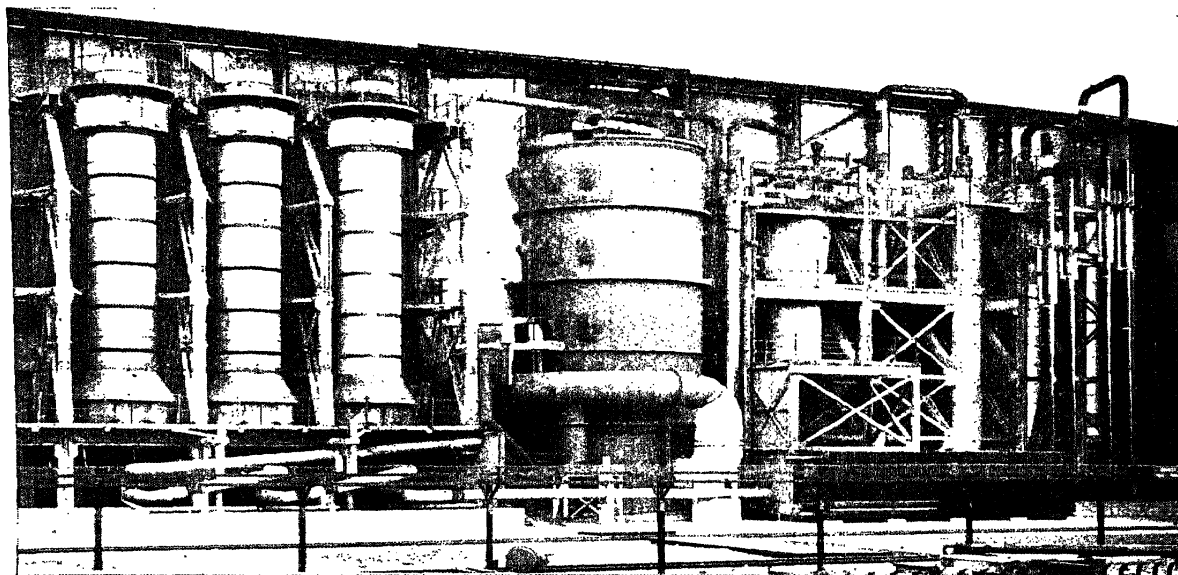
FIGURE 155.—A view of a unit in the coal and tar hydrogenation plant at Billingham-on-Tees, England. At the left, 3 converters in which the paste-in-oil receives hydrogen under pressure; in the center, the preheater; next, a gas-liquid separator. To the right, heat exchangers. The brick wall behind the unit is for the protection of the rest of the plant, in case of fire. (By courtesy of the Imperial Chemical Industries, Fertilizer and Synthetic Products, Ltd., Billingham, Co. Durham.)

In England, the hydrogenation of bituminous coal, and of tar products from by-product coke ovens and coking retorts for city gas plants, is an established process; it is expected that there will be produced annually 30 million imperial gallons of motor fuel from coal, and 15 million gallons more from various tar products.[43] Since gasoline is 85 per cent carbon and 15 per cent hydrogen, while coal has for each 85 parts, only 5 parts hydrogen, it is hydrogen to the extent of 10 parts per 90 parts of coal which must be introduced. The process is a coal-in-oil phase which is pumped to the converter under pressure; the temperature is raised to 390° C. (734° F.) for half an hour, then to 450° C. (842° F.) for one hour.

[42] U. S. Patent 1,592,772, to Friedrich Bergius.
[43] "Coal hydrogenation at Billingham," *Chem. Met. Eng.*, **42**, 658 (1935), with 7 illustrations and 2 flow-sheets.

The product is separated into a heavy oil portion, which is hydrogenated further, the motor fuel fraction, and unreacted coal (5 per cent).

A synthetic motor fuel is methanol, made catalytically from carbon monoxide or dioxide with hydrogen. By changing the catalyst, the same raw materials yield a mixture of higher-boiling liquids which would be suitable for motor spirits; it is called Synthol.

Industrial alcohol has been discussed in Chapter 20, and is suitable if mixed with petroleum distillates and blending agents. Alcohol alone may be used, but a special carburator is required. Alcohol with 33 per cent sulfuric ether, however, is suitable for the regular gasoline carburator, after recoating its float with an alcohol- and ether-resisting skin. Such a motor fuel has become of importance in the warm countries, where molasses is available at a low price. The alcohol is changed partly into ether, as explained in Chapter 30, and plants with continuous operation and a capacity of 3000 gallons daily are in operation. A small amount of a basic denaturant such as pyridine is part of the formula. The "alcoleter" of Cuba is such a motor spirits.

Oil shales are still another possible source.[44]

LUBRICANTS

The present-day lubricating oils are mainly the mineral oils refined as described under paraffin distillate. Blends of mineral and fatty oils, vegetable or animal, are used to a considerable extent, particularly in cutting oils in the machine shop. Soluble cutting oils are emulsified with water and cool as well as lubricate; they contain sulfonated oil with mineral oil. Formerly castor, lard, coconut, olive, and many other oils were used without additions; several fatty oils are still in great demand for blended lubricating oils, rape oil for example.

The thickest oil obtained from the paraffin fraction may serve for steam cylinder oil, but it usually is blended with fatty oils for such service. Lubricating agents of still higher viscosity are the greases, a calcium or sodium soap jelly emulsified with much mineral oil, and usually containing a little water. Graphite by itself and mixed with greases is a lubricator; an outline for the preparation of such a mixture will serve for that of greases in general, although only one grease in a hundred contains graphite.

Tallow is pumped (melted by steam lines) into a kettle 10 feet high and 6 feet wide, fitted with slowly rotating, scraping agitators; the kettle is steam jacketed and of cast iron. A high-grade hydrated lime is added in amount sufficient to form the calcium salt of the fatty acids in the tallow; the glycerin formed [45] at the same time is not removed. When the soap has formed, warm mineral oil in which the graphite has previously been suspended is poured in and the whole mass well mixed; while warm it is comparatively fluid. It is run off from the bottom of the

[44] "Shale oil," by R. H. McKee, New York, Chemical Catalog Co., Inc., 1925.
[45] Chapter 32.

kettle to barrels and cans on a lower floor. The content of calcium soap varies from 10 to 25 per cent, of graphite 2 to 5 per cent (occasionally more up to 25 per cent), of water 1 to 3 per cent, and the balance mineral oil. The grade of oil used would pass through the Saybolt viscosimeter [46] in 150 seconds at 100° F. or 37.80° C. (60 cc.); this would be an average. The variation, to suit various demands, is from 100 to 200 seconds. A sodium soap jelly base is preferred when heat from the outside may reach the lubricated parts.

Wagon axle grease and railroad curve grease are made by the cold reaction of rosin oil [47] and hydrated lime previously suspended in mineral oil. The hard locomotive cup grease, which must be turned down with a wrench, is made by mixing tallow and oil and pouring in a concentrated solution of caustic soda. The reaction takes place in the cold;[48] the mass sets into a solid.

TABLE 49.—*Percentage Yields of Refined Products, Computed on Total Crude Run to Stills.*

	1924	1934	1935
Gasoline**	31.2	43.4	44.2
Kerosene	9.3	6.0	5.8
Gas oil distillate fuel oil	} 49.8	10.6	10.4
Residual fuel oil		26.8	26.4
Lubricants	4.3	2.9	2.9
Wax	.3	.2	.2
Coke	.6	.7	.8
Asphalt	2.2	1.7	1.8
Road oil	n.r.***	.7	.7
Still gas	n.r.	5.0	5.2
Other finished products	1.3	.2	.2
Shortage	3.0	1.8	1.3

* Bureau of Mines.
** Based on total gasoline produced less natural gasoline.
*** No record.

A distinction can be made between hand lubrication, cup lubrication and bath lubrication; the automobile motor has circulating bath lubrication. Lubricants are used to form a film on a rotating metal (shaft) which in turn rests on the stationary bearing; the shaft is really carried by the film. The film must not break; it must have body enough not to be squeezed out by the load; it must have these properties at the temperature at which it works. In general the viscosity is a measure of the lubricating power.[49]

Paraffin-base lubricating oils are improved by mixing with them 1 per cent of Paraflow.[50]

The production of refined petroleum products is given in Table 50.

[46] "Standard methods of chemical analyses," W. W. Scott, New York, D. Van Nostrand Co., 1925.
[47] Chapter 31.
[48] See "Lubricating greases," by E. N. Klemgard, New York, Chemical Catalog Co., Inc., new edition, 1937.
[49] For theory of lubrication, see "The technical examination of crude petroleum, petroleum products, and natural gas," W. A. Hamor and F. W. Padgett, New York, McGraw-Hill Book Co., 1920, p. 119.
[50] U. S. Patent 1,815,022, or *Ind. Eng. Chem.*, 23, 1452 (1931).

TABLE 50.—*Production (U. S.) of the Major Refined Products from Crude Oil, in Thousands of Barrels of 42 Gallons, Except for Wax, Which is Given in Thousands of Pounds.*

	1924	1934	1935	1936
Motor fuel	215,529	423,801	465,514	515,485
Kerosene	60,026	53,855	55,813	56,082
Gas oil, fuel oil	320,476	335,353	355,125	411,338
Lubricants	27,498	26,373	27,771	30,905
Wax	516,491	468,720	450,240	472,920

* Bureau of Mines.

The following prices are from miscellaneous sources but will serve as guides in estimating the relative money value of petroleum products: Crude oil, Oklahoma 34° A.P.I., $1.20 a barrel, end of 1935; lubricating oil, end of 1935, 17 cents a gallon; bunker oil, end of 1935, 95 cents a barrel; kerosene, almost 8 cents a gallon; natural gas gasoline, average price over the year of 1935, 3.34 cents a gallon. Standard gasoline in July, 1937, was quoted at 9.5 to 10 cents per gallon, in tank cars, at the refinery. All these prices are for bulk, on contract.

Tests for Petroleum Oils. Special tests are used for oils. Gasolines are tested for their boiling range to the very last drop (the final temperature is called the dry point), and for their octane number. Gasoline and kerosene are both tested for specific gravity, color, clarity. Any oil to be used as fuel oil is tested among other ways for its heat value, in a calorimeter. Diesel oils are tested for the cetane number, in addition to the usual oil tests. Lubricating oils are tested for their viscosity especially; in the Saybolt viscosimeter, the time required for a definite volume at a certain temperature to pass through a standard orifice is recorded. Viscosities for two different temperatures lead to the viscosity index. The flash point is the lowest temperature at which an oil vapor with the surrounding air forms a mixture which flashes when a small pilot light is applied; the flash test is performed for kerosene and lubricating oils especially. There are many other tests which will be found described in the chemical handbooks and in textbooks on analytical chemistry.

OZOKERITE

Ozokerite is a mineral wax which occurs in Utah, Colorado, and in Galicia; it is of petroleum origin. It may be purified by melting, decanting from insoluble matter and decolorizing by running the liquid through charcoal. Another method is to extract the wax by benzene. The hardest wax is made from it by a German process. The crude wax is melted and kept warm 4 hours till anhydrous; at 120° C. 20 per cent of fuming sulfuric acid is added, gradually, and the heating continued till all the fumes have passed over. The liquid wax forms an upper layer over the impurities which gradually become granular and settle; the liquid is decanted, freed from acid by stirring in charred blood, decolorized by animal charcoal or silica, and filtered. The color is then yellow, instead of the original black. If white wax is sought, the process is repeated. The product is ceresin,

which serves as a substitute for beeswax. It is highly prized for making candles, and serves the chemical trade for small containers for hydrofluoric acid.

In still another process, the crude wax is distilled with superheated steam, yielding a white wax melting at 140° F. (60° C.), light oil, and a semi-solid wax used in the perfumery industry. The residue in the still is black; mixed with raw rubber, and vulcanized, there is formed okonite, a flexible, tough, water-proof insulator.

ASPHALT

Asphalts are solid native bitumens (that is, hydrocarbons) which melt on heating to the temperature of boiling water, or near it. Trinidad Lake asphalt is a solid bitumen found naturally mixed with silica and clay; it occurs in just that form only on the island of Trinidad. Other asphalts are found impregnating amorphous limestone, crystalline limestone, or shales, in Europe (Sicily and other localities), in Oklahoma, Utah, and California. The asphalts are used for paving cements, and for this purpose are frequently softened by the addition of residues from the distillation of various crude oils.

OTHER PATENTS

U. S. Patent 1,848,054, dewaxing petroleum fractions by filtering under differential pressure; 1,800,887, breaking petroleum emulsions; 1,814,042, continuous transformation of petroleum hydrocarbons into gasoline and coke-like complexes, without the formation of fuel oil; 1,848,681, antiknock gasoline, by cracking oils at high temperatures; 1,838,449 and 1,768,521, absorption of gasoline from natural gas, by oil scrubbing; 2,074,338, a lubricant comprising in combination a mineral oil and a halogenated higher fatty acid of the aliphatic series; 1,937,759, on the art of refining; Canadian Patent 339,404, wax separation from oil; 339,405, hydrocarbon oil stabilization; U. S. Patent 2,032,666, stabilization of light hydrocarbon oil and particularly pressure distillate; 2,032,662, desulfurizing gasoline; 2,032,680, process of varying the bitumen content of rock asphalt; 2,038,599, 2,039,259, carrying out catalytic reactions, to M. Pier and P. Jacob; 1,946,108, production of catalysts; 2,068,979, method of preventing corrosion in oil stills, by adding an oil soluble naphthenate; 1,955,272, on the recovery of aluminum chloride from the residue of aluminum chloride refining; 1,955,260, to produce "synthetic lubricating oils" from paraffin wax, cracking, then polymerizing with catalysts, followed by an aluminum chloride treatment; 2,069,170, refining mineral lubricating oil by propane vapors; 2,069,173, refining hydrocarbon gases, with liquid SO_2, separating unsaturated from saturated; British Patent 442,429, use of an electrical field to coagulate separated asphalt from the oil; U. S. Patent 2,038,798, furfural as extracting solvent; 2,027,346, propylene dichloride and ethylene glycol ethyl ether as solvent for the oil and not the wax; 2,028,361, phenol, aniline, and other selective solvents; 2,040,239, on liquefied propane as precipitant of the asphlatic impurities; other patents on the use of certain solvents for the purification of lube stock are 2,054,433, 2,055,428, 2,049,277, 2,047,826, 2,041,885, 2,043,389; also Canadian Patent 343,452.

PROBLEMS

1. A storage tank for gasoline, with closed top equipped with a patent breathing valve, is 60-feet circular in diameter and 40 feet in height. It is designed for gasoline testing 55° A.P.I. at 60° F./60° F. How many gallons will it hold? How many gallons per inch of height? A table of A.P.I. degrees and corresponding specific gravity will be found in the appendix.

2. In a "bulk plant," there is a storage tank 35-feet high, 25 feet in circular

diameter, for the storage of kerosene of 40° A.P.I. at 60° F./60° F. How many gallons will it hold, and how many gallons for an inch of height?

3. In the same "bulk plant," another cylindrical tank is 25 feet in diameter and 30 feet in height. It holds a fuel oil testing 36° A.P.I. at 60° F./60° F. What is the capacity of the tank for this oil, and how many gallons per inch will it hold?

4. A pipe line delivers 5500 barrels of oil to a refinery in one day, at a regular rate over the 24-hours. The line is an 8-inch line. The oil is stored in 3 receiving tanks which are circular in cross-section, and 12-feet high. What size will the tanks have to be to hold one day's delivery. What is the velocity of the oil in the pipe, in feet per second? (Velocity × area — discharge.)

5. From the table of "Percentage yield of refined products" in the text, which represent weight relations, take the figures for each year and tabulate how much product by weight you would have produced every day from a daily crude input of 7800 gallons. For the gasoline, kerosene, and fuel oil items, compute the volume, taking the A.P.I. densities as given in problems 1, 2, and 3.

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There was a time not so long ago when the chemist sought exclusively for natural products so that he might extract or distill from them the complicated molecules containing carbon, hydrogen, and oxygen or nitrogen. The distillates or extracts were chemicals originating in nature's laboratory, in living systems, vegetable or animal; they were therefore called "organic." It was with reverence that the chemist isolated such chemicals. To-day, he is bolder. Natural sources are still sought and utilized, but in addition, the chemist or engineer uses coal and limestone, for example, and produces from them the delicate and volatile acetate esters. This makes true the slogan: From rocks to ethereal solvents. But it is well to note at once that even in these bold syntheses, all the worker does is to provide the circumstances and conditions so that the laws of nature may function to his advantage. At no time does he make nature do his will; the achievement is rather in the discoveries of a few of those laws; the attitude of humility before the decreasingly mysterious laws of nature is still in order.

Chapter 25

Synthetic and Semi-Synthetic Organic Chemicals

In the course of the three decades, now past, in this century, and particularly since the war emergency, a number of organic synthetic chemicals has been brought to the commercial state and has entered the economic life of the world. The best known are the compounds derived from acetylene; by catalytic hydration, acetaldehyde is formed, and this in turn, by catalytic oxidation, yields acetic acid. This is synthetic acetic acid, able to replace in all its uses the older acetic acid from wood distillation. Of more recent date, and perhaps less well known, are the chemicals built on ethylene $CH_2:CH_2$ as starting material; they include ethylene glycol and the glycol ethers. The ethylene derivatives are manufactured mainly by straightforward chemical reaction, and only in rare instances, by contact catalysis. If it had not been for this important group of ethylene derivatives, the chapter might have been entitled: Contact Catalysis Processes. A third important starting material is carbon monoxide, which reacts with hydrogen, in contact with a properly chosen catalytic agent, to form methane CH_4, or methanol CH_3OH and higher alcohols, according to the nature of the catalyst and other conditions.

The three series listed in the previous paragraph represent synthetic chemicals. What might be called semi-synthetics are chemicals resulting from partial or controlled oxidation of natural products, chiefly again with the aid of a contact substance; for example, phthalic anhydride from naphthalene. Another semi-synthetic group would be the hydrogenated vegetable oils which become "vegetable fats," due to the addition of hydrogen to the molecule.

A number of synthetic and semi-synthetic substances, of value in the perfume industry, will be found described in Chapter 30. Synthetic amyl alcohol from pentane is included in Chapter 20.

CHEMICALS BASED ON ACETYLENE AS STARTING MATERIAL

Acetylene is the gas formed by the action of water on calcium carbide, a product of the electric furnace. The early use of the gas was as an illuminant, about 30 years ago, when its dazzling white light was

TABLE 51.—*Relation of the Acetylene Chemicals,* [1] *First Part*

$$CH : CH \xrightarrow{+HOH} CH_3.CHO \xrightarrow{+O} CH_3COOH$$

acetylene (gas)   acetaldehyde (volatile liquid)   acetic acid (liquid)

$$+HCl \quad (Cu_2Cl_2, NH_4Cl) \qquad +H_2 \qquad less\ H_2O\ and\ CO_2 \qquad less\ H_2O$$

$$CH_2 : CHCl \qquad C_2H_5OH \qquad CH_3.CO.CH_3 \qquad (CH_3CO)_2O$$

vinyl chloride (gas)   ethyl alcohol (liquid)   acetone (liquid)   acetic anhydride (liquid)
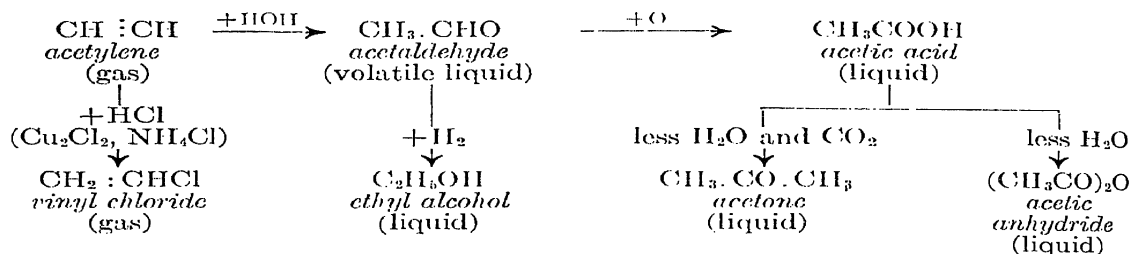
highly prized. Its high heat of combustion led to its use in welding and cutting torches. It is now generated and fed into a suspension of mercurous sulfate in water or dilute sulfuric acid, where it is a chemical, which attaches a molecule of water to each one of its molecules, to form acetaldehyde. By oxidation, acetic acid is then formed, and this in turn may serve as a source for acetone. By hydrogenation, acetaldehyde

TABLE 52.—*Relation of the Acetylene Chemicals, Second Part.*
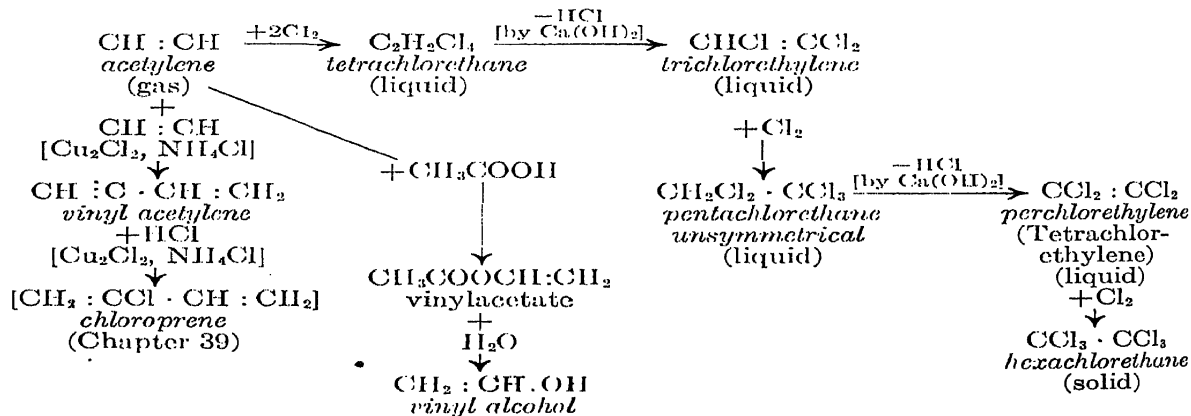
$$CH : CH \xrightarrow{+2Cl_2} C_2H_2Cl_4 \xrightarrow[\text{[by Ca(OH)}_2]}{-HCl} CHCl : CCl_2$$

acetylene (gas)   tetrachlorethane (liquid)   trichlorethylene (liquid)

+ CH : CH [Cu_2Cl_2, NH_4Cl]

$$CH : C \cdot CH : CH_2$$

vinyl acetylene   + CH_3COOH $+Cl_2$

+HCl [Cu_2Cl_2, NH_4Cl]

$$CH_2Cl_2 \cdot CCl_3 \xrightarrow[\text{[by Ca(OH)}_2]}{-HCl} CCl_2 : CCl_2$$

[CH_2 : CCl · CH : CH_2]   pentachlorethane unsymmetrical (liquid)   perchlorethylene (Tetrachlorethylene) (liquid)

chloroprene (Chapter 39) $CH_3COOCH:CH_2$ +Cl_2

vinylacetate $CCl_3 \cdot CCl_3$

+ H_2O   hexachlorethane (solid)

$$CH_2 : CH.OH$$

vinyl alcohol

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gives ethyl alcohol, an actual source of this material. The relation between acetylene and the products based on it is shown in Tables 51 and 52.

Acetaldehyde. Acetylene [1a] is generated from calcium carbide by the action of air-free water in a series of generators feeding a central holder. The gas from the holder enters the reaction vessel made of Duriron, conical in shape, and surmounted by a short plate column. A quantity of liquid is contained in the cone bottom of the reaction vessel, and contains water, acetaldehyde, and mercurous sulfate in suspension. The gas enters at the bottom at a steady rate and keeps the thin sludge well stirred. At a corresponding rate, air-free, lukewarm water is fed in. At definite intervals, a part of the sludge is removed, and a charge of fresh mercurous sulfate suspended in air-free water is supplied. The reaction $C_2H_2 + H_2O = CH_3CHO$ is exothermic, so that heat must be removed by cold water circulating in a coil placed in the reaction vessel. The temperature is maintained at 68° C. (154° F.) at which acetaldehyde passes out freely, carrying with it a certain amount of water vapor. In the plate tower, cooling causes condensation of a water solution of aldehyde, which becomes stronger the higher the plate. There passes out at the top acetaldehyde, water, acetylene, and several other minor reaction products in smaller quantities; the vapors pass upward in a circular box with cooling coils. A water solution of acetaldehyde containing about 20 per cent water is collected and stored in aluminum tanks; the acetylene gas passes out and after purification joins the makeup gas on its way to the reaction vessel. Pure acetaldehyde boils at 20° C. (68° F.) at atmospheric pressure.

Acetic Acid. From acetaldehyde directly, several chemicals are formed: acetic acid, ethyl acetate, butyl acetate, acetic anhydride, while acetic acid and acetylene may be made to yield acetic anhydride, all by catalytic reactions.

For acetic acid, a batch process [2] is used. A thousand gallons of acetaldehyde from the acetylene hydration, rectified so that its water content is very low, are pumped into an aluminum-lined reaction vessel provided with coils for water or steam. To this 0.5 per cent manganese sulfate or acetate is added, and air (300 cu. ft. per minute) blown in against the pressure at which the reaction vessel is operated, about 3 atmospheres. The temperature is raised to 25° C. (77° F.), which is below the boiling point of acetaldehyde at the pressure used. As the reaction gets under way, the temperature rises to 65° C. (149° F.) and the pressure to 75 pounds. $2CH_3.CHO + O_2 = 2CH_3.COOH$. Nitrogen is allowed to escape through a brine-cooled separator, which retains the entrained aldehyde and acid. The reaction is complete in 8 to 12 hours, when the charge is distilled, then redistilled with the aid of a plate column, operated continuously and yielding 99 per cent acetic acid.

The function of the mangenese catalyst is not to catalyze the oxidation of the aldehyde, but rather to decompose an intermediate prod-

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[1a] For other sources, see brief statement in chapter 19.

[2] English Patent 132,558 (1918), class II, 3, p. 91 abridgements; 132,557 (1918), class II, 3, p. 90 abridgements.

uct, per-acetic acid, which is explosive; as it decomposes, the desired acetic acid forms. The higher manganese oxide formed attacks fresh acetaldehyde.

$$CH_3.CHO + O_2 = CH_3.CO.O.OH$$
per-acetic acid

$$CH_3.CO.O.OH + MnO_2 = CH_3.COOH + MnO_3 \text{ or intermediate oxides}$$
brown color

$$MnO_3 \text{ or intermediate oxides} + CH_3.CHO = CH_3.COOH + MnO_2$$
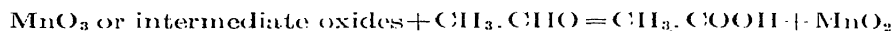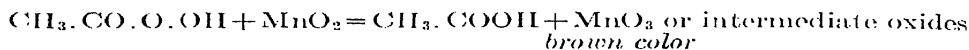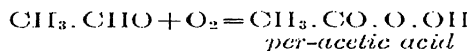
Ethyl Acetate from Acetaldehyde. In the presence of small amounts of aluminum ethylate $Al(C_2H_5O)_3$ and aluminum chloride $AlCl_3$, acetaldehyde is transformed to ethyl acetate with a recovery of over 90 per cent. $2CH_3CHO = CH_3.COOC_2H_5$. At the present time, ethyl acetate is made almost exclusively from fermentation alcohol and acetic acid from various sources, but the process just given may gain industrial importance in the future.

Acetic Anhydride from Ethylidene Diacetate. If instead of passing acetylene into a water suspension of mercurous sulfate, as is done in the fundamental process in this series, it is passed into a suspension of mercurous sulfate in concentrated or glacial acetic acid, using the same kind of reaction vessel, there is formed ethylidene diacetate. (The ethylidene radicle is $CH_3CH:$). $C_2H_2 + 2CH_3.COOH = CH_3CH(O.CO.CH_3)_2$.

On distilling this product in the presence of small quantities of anhydrous salts or agents, such as zinc chloride or sodium pyrophosphate $Na_4P_2O_7$, the diacetate decomposes into acetaldehyde and acetic anhydride. $CH_3.CH(O.CO.CH_3)_2 = CH_3.CHO + O(CO.CH_3)_2$.

The distillation may be performed at reduced pressure (100 mm.) and 80° C. (176° F.), or at atmospheric pressure and 130° C. (266° F.). The acetaldehyde may be used over again in the acetic acid synthesis.

It has been found advantageous to introduce the decomposing agent, such as phosphoric acid, in small lots [3] at suitable intervals to the boiling ethylidene acetate, in order to avoid forming acetic acid or tars. The conversion is 87.4 per cent. In the subsequent distillation, unchanged ethylidene acetate is left behind; the distillate is fractionated and furnishes 80 to 90 per cent acetic anhydride, the customary commercial strength.

Acetic Anhydride from Acetic Acid. Acetic anhydride may be made directly from glacial acetic acid by passing it in vapor form over granules of catalyst [4] kept at 600° to 620° C. (1112° to 1148° F.). The catalyst is made by mixing 200 grams of sodium ammonium phosphate $NaNH_4HPO_4$ with 1000 grams boron phosphate; the yield is 48 to 50 per cent.

The standard method for acetic anhydride manufacture will be found in Chapter 16.

[3] U. S. Patent 1,578,454.
[4] U. S. Patent 1,870,357.

The United States production of acetic acid (1931) in the form of acid less concentrated than 100 per cent was 48,846,511 lbs., calculated to the 100 per cent basis; that for glacial acetic acid, 13,739,589 lbs. Both average 5.65 cents in price.

Chlorinated Hydrocarbons. By the chlorination of acetylene to tetrachlorethane, followed by the removal of hydrogen chloride, trichlorethylene is formed. It is a liquid which has become an important solvent. It is now made at the rate of many tons a day. By chlorination, with a subsequent hydrogen chloride removal, and again chlorination, three more chlorinated hydrocarbons are formed, as shown in Table 52.[4a]

Another important branch of the acetylene chemicals family are the vinyl compounds. A stream of acetylene in acetic acid gives *vinylacetate*, which may then be hydrolized to give *vinyl alcohol;* this substance is readily polymerized [4b] to various degrees, and products of different viscosities are obtained. Vinyl alcohol is used to diminish the "drag out," that is, the volume of liquid carried out by the metal objects on being removed from the bath. There is a growing list of other uses.

Acetylene to form chloroprene, 2-chlor-1, 3-butadiene, is presented in chapter 39.

Degreasing Metal Surfaces. An important use of certain of the newer solvents is in the degreasing of metal surfaces, preparatory to coating them with another metal, by electrolysis, by dipping, or in some other way. Trichlorethylene particularly is favored, and not only its uses, but several methods for performing the degreasing, with the apparatus, have been the subject of patents.[4c] In one system, the cold metal parts are suspended in the vapor of the solvent, which recondenses on the walls of the same vessel, extended to form a short reflux column; only the pure solvent, with maximum solvent power, reaches the objects. The solvent is kept warm by a steam coil. The vapors do not escape thanks to their great weight relative to air. In order to prevent corrosion, a "stabilizer" is added; this may be 0.001 per cent triethylamine,[4d] 0.05 per cent to 0.1 per cent amylene,[4e] or, less satisfactory, gasoline.[4f]

SYNTHETICS WITH ETHYLENE AS STARTING MATERIAL

An important series of valuable organic compounds has been realized, chiefly by the brilliant work of American chemists and chemical engineers, by the building up of the molecule of ethylene, $CH_2:CH_2$. The family tree in Table 53 exhibits the relation between the more important members of this series. Ethylene is an unsaturated compound, which readily forms addition products. The additions which are of service here are hypochlorous acid or chlorine, followed by reactions

[4a] *Compare* "An R. & H. Technical Bulletin," "Chlorinated Hydrocarbons," (1935), The R. & H. Chemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.
[4b] U. S. Patent 1,942,531, to Dr. Harold Barrett.
[4c] U. S. Patents 1,906,968; 1,961,867; 1,875,937; 1,938,841; 1,869,845; and 1,869,826.
[4d] U. S. Patent 1,911,926.
[4e] U. S. Patent 1,904,450.
[4f] U. S. Patent 1,816,895.

TABLE 53.—*Ethylene and its Derivatives of Industrial Importance.*

CH_2 \ CH_2 / *ethylene* (gas) — HOCl → CH_2OH CH_2Cl *ethylene chlorhydrin* (liquid) — NaHCO$_3$ → CH_2OH CH_2OH *ethylene glycol* (liquid)

CH_2OH $CH_2OC_2H_5$ *mono-ethyl ether of ethylene glycol* (liquid)

CH_2OH CH_2OCH_3 *mono-methyl ether of ethylene glycol* (liquid)

CH_2 \ O CH_2 / *ethylene oxide* (low boiling liquid)

CH_2OH $CH_2OC_2H_5$ *mono-ethyl ether of ethylene glycol* (liquid)

CH_2CH_2Cl O CH_2CH_2Cl *di-chlor-ethyl ether* (liquid)

CH_2OH CH_2 O CH_2 CH_2OH *di-ethylene glycol* (liquid)

CH_2OH CH_2 O CH_2 $CH_2OC_2H_5$ *mono-ethyl ether of di-ethylene glycol* (liquid)

CH_2 NO_3 CH_2 O CH_2 $CH_2.NO_3$ *di-ethylene glycol di-nitrate* (liquid)

CH_2OH CH_2 O CH_2 CH_2 O CH_2 CH_2OH *tri-ethylene glycol* (liquid)

CH_2 \ O CH_2 / *ethylene oxide* (liquid)

$CH_2.O.CH_2$ $CH_2.O.CH_2$ *dioxan* (liquid)

$CH_2.NO_3$ $CH_2.NO_3$ *glycol di-nitrate* (liquid)

CH_2OH $CH_2OOC.CH_3$ *mono-acetate of ethylene glycol* (liquid)

$CH_2OOC.CH_3$ $CH_2OOC.CH_3$ *di-acetate of ethylene glycol* (liquid)

CH_2 \ CH_2 / *ethylene* (gas) — steam → CH_3 CH_2OH *ethyl alcohol*

CH_2 \ CH_2 / *ethylene* (gas) — NH$_3$ → $CH_2.NH_2$ $CH_2.NH_2$ *ethylene diamine* (liquid)

HO.CH_2.CH_2.NH_2 *mono-ethanolamine* (liquid)

HO.CH_2.CH_2 \ NH HO.CH_2.CH_2 / *di-ethanolamine* (liquid)

HO.CH_2.CH_2 HO.CH_2.CH_2—N HO.CH_2.CH_2 *tri-ethanolamine* (liquid)

CH_2 \ CH_2 / *ethylene* (gas) — Cl$_2$ → CH_2Cl CH_2Cl *ethylene chloride* (liquid) — NaOOC.CH$_3$ (in alcohol) → $CH_2.OOC.CH_3$ $CH_2.OOC.CH_3$ *glycol di-acetate* (liquid)

CH_2OH CH_2OH *ethylene glycol*

$CH_2.NH_2$ $CH_2.NH_2$ *ethylene diamine* (liquid)

$CH_2.CN$ $CH_2.CN$ *ethylene di-cyanide* → $CH_2.COOH$ $CH_2.COOH$ *succinic acid* (solid)

$CH_2.OH$ $CH_2.OH$ *ethylene glycol*

CH_2 $CH.Cl$ *vinyl chloride* (gas) → *vinylite resins*

which replace the halogen by a hydroxyl (OH), an ethoxy (OC$_2$H$_5$) or other alkyloxy group, or an acetyl radicle (OOC.CH$_3$), or reactions which remove hydrogen chloride or water. The central substance is ethylene glycol OH.CH$_2$.CH$_2$.OH, a liquid, manufactured at the rate of 30 tons a day.

Ethylene. The gas ethylene is obtained in the large amount required for this industry from oil, cracked in the vapor phase (Gyro), or from cracked natural gas; fair quantities are also present in coke-oven gas. It is obtained in the pure state by compressing the raw gas to several atmospheres and treating this with acetone in an absorption tower [5] (*see* Fig. 156). Acetone is forced in at the top and travels downward over the several plates. The gas travels upward, bubbling through the solvent, in which the ethylene dissolves. An acetone solution rich in ethylene collects at the bottom of the tower, and is sent
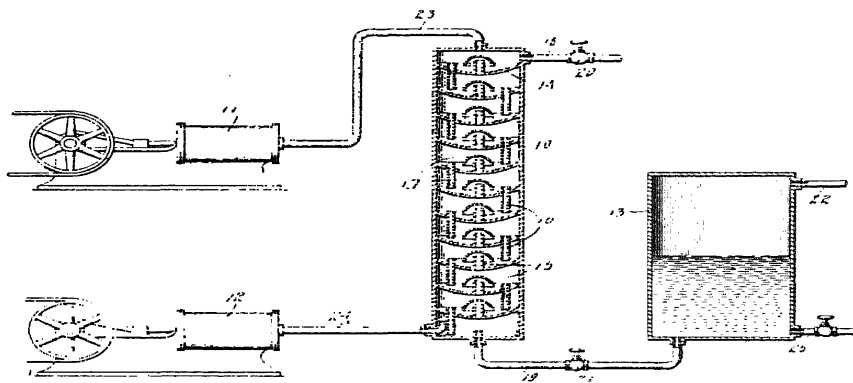
Figure 156.—Plant for the extraction of ethylene from a gas mixture, showing absorption tower, separating chamber, and the two compressors. (From the patent.)

to an expansion chamber, where the pressure is released; the pure gas escapes from the liquid and is drawn off through a line at the top of the chamber. The liquid below is used over again, or, when maximum production is needed, is warmed and passed through a short plate tower; the residual ethylene is thus recovered. The acetone is then ready for a new absorption cycle. The pure ethylene gas is collected in a holder from which it is drawn as needed.

Ethylene is obtained from ethyl alcohol, by catalytic dehydration; this was the method used during the war emergency (Chapter 34).

Ethylene Chlorhydrin. In the next step, ethylene forms an addition compound with hypochlorous acid HOCl in water solution,[6] the chlorhydrin formed, OH.CH$_2$.CH$_2$.Cl, remaining also in solution in the water. Inasmuch as hypochlorous acid is not stable, its sodium salt,

[5] U. S. Patent 1,422,184.
[6] U. S. Patent 1,456,916.

sodium hypochlorite NaOCl, is prepared, and the free acid liberated only at the moment it is to react.

Chlorine gas is passed into a solution of iron-free caustic soda, kept at 10° C. (50° F.), in order to avoid chlorate formation. The reaction $2NaOH + Cl_2 = NaOCl + NaCl + H_2O$ takes place. Enough chlorine is passed in so that no free alkali remains; the strength is adjusted at 5 to 7 per cent NaOCl. The vessel and pipes are of chemical stoneware.

The hypochlorite solution passes to the first decomposing cell (3 in Fig. 157), maintained at 0° to 10° C. (32° to 50° F.), where it meets a stream of chlorine gas in quantity sufficient to react with most, but not all, of the sodium hypochlorite: $NaOCl + Cl_2 + H_2O = 2HOCl + NaCl$. The solution of hypochlorous acid now passes through a cooling coil to the bottom of the first reaction tower (8 in the sketch). Ethylene gas enters through a porous plate in the base of the tower, so that it is divided into fine bubbles. A quantity of liquid several feet in height is
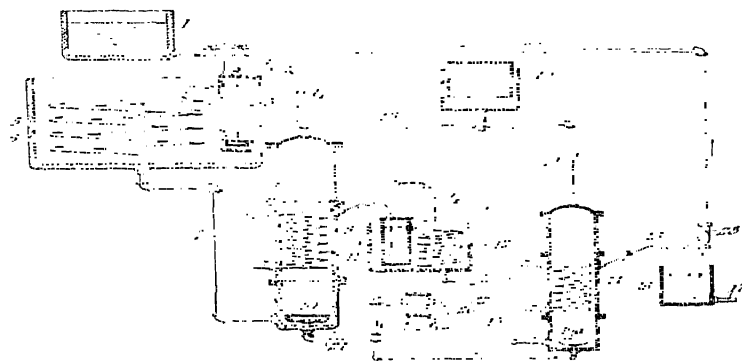
FIGURE 157.—Absorption of ethylene in hypochlorous acid to form the chlorhydrin. 3 and 9, chlorinating cell to form hypochlorous acid; 8 and 14, reaction towers; 10 and 10a, inlets for ethylene gas; 1, storage for sodium hypochlorite solution. (From the patent.)

kept in the tower, and through this, the gas rises, combining with the free hypochlorous acid. $C_2H_4 + HOCl = OH.CH_2.CH_2.Cl$. The reaction is exothermic; by means of the coils placed in the tower, brine may be circulated, and this heat removed, so that the temperature is maintained close to 0° C. (32° F.).

A portion of the liquid in the tower is allowed to overflow into the second decomposition cell (9 in sketch), placed in a brine tank. In this cell a fine stream of chlorine enters and decomposes the remaining sodium hypochlorite; this solution passes through a cooling coil again, and enters the second reaction tower, again forming a body of liquid through which ethylene gas is allowed to rise in fine bubbles. The overflow from this tower reaches an intermediate tank; a portion is sent to join the fresh sodium hypochlorite liquor for the first cell, serving as diluent. The main part is drawn off and purified; the impurities are sodium chloride, a small amount of hydrochloric acid, and traces of hypochlorous acid and of chlorate. A slight excess of sodium bisulfite is added to destroy the latter two substances, and calcium carbonate to neutrality. The liquid obtained may contain as much as 20 per cent

ethylene chlorhydrin; it is concentrated further by distillation, usually to the 42.3 per cent strength, because this is a constant boiling mixture.

This procedure has been improved [7] (*see* Fig. 158) by circulating a larger proportion of the chlorhydrin solution, and injecting only enough sodium hypochlorite solution to produce 0.1 per cent hypochlorous acid in the liquid fed the reaction tower; in fact, the customary concentration is 0.06 per cent. One part of hypochlorite solution is added to 80 to 250 parts of recirculated liquor. A stream of chlorine sufficient to decompose 50 to 80 per cent of the sodium hypochlorite is injected into the circulating liquor pipe. A definite amount of liquor is discharged constantly and worked up for its chlorhydrin content.

FIGURE 158.—Improved procedure for the absorption of ethylene in hypochlorous acid. In each reaction tower (1 and 12), the chlorhydrin solution is circulated, with injection of small amounts of sodium hypochlorite (at 8) and of chlorine (at 10 and 19). (From the patent.)
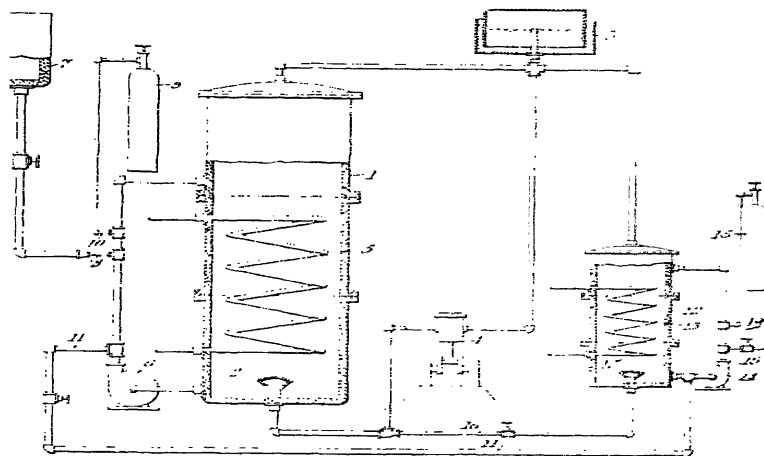
Ethylene Glycol. Ethylene chlorhydrin is transformed into ethylene glycol by means of a solution of sodium bicarbonate.

$$OH . CH_2 . CH_2 . Cl + NaHCO_3 = OH . CH_2 . CH_2 . OH + NaCl + CO_2 \qquad (1)$$
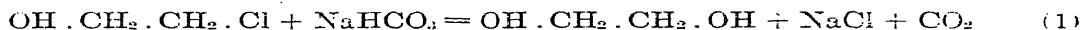
The apparatus [8] (*see* Fig. 159) consists of two closed kettles, steam-jacketed and with stirrer; and two storage tanks, one for a caustic solution, one for the chlorhydrin solution. The caustic solution is made 20 per cent NaOH, the chlorhydrin 40 per cent $OH.CH_2.CH_2.Cl$. Caustic solution is run into kettle 2, and carbon dioxide passed in, to form the bicarbonate. $NaOH + CO_2 = NaHCO_3$. A charge of chlorhydrin solution, in amount just right to follow equation (1), is run in, and the temperature slowly raised to 70° C. (158° F.) while stirring. The reaction starts and proceeds smoothly; it is complete in 4 hours. The gas evolved (CO_2) is passed into kettle 1, which contains its charge of caustic solution, so that bicarbonate for the next batch is being made by the same gas.

It is necessary to guard against losses in the form of ethylene oxide; these are minimized by starting with the cold caustic.

[7] U. S. Patent 1,456,959.
[8] U. S. Patent 1,442,386.

The weak glycol solution obtained is concentrated by heating in a vacuum, water vapors passing out. When completely dehydrated it is a somewhat viscous liquid, very hygroscopic, boiling at 197.2° C. (387° F.). It is miscible with water in all proportions, causing a drop in the freezing point of the solution; 60 per cent ethylene glycol and 40 per cent water have the minimum freezing point, −49° C. (−56° F.), hence its value as an antifreeze in automobile radiators.

A new method other than the following ones, which will supercede the hypochlorous acid-bicarbonate method for making ethylene glycol from ethylene has been developed, and its details are being patented.
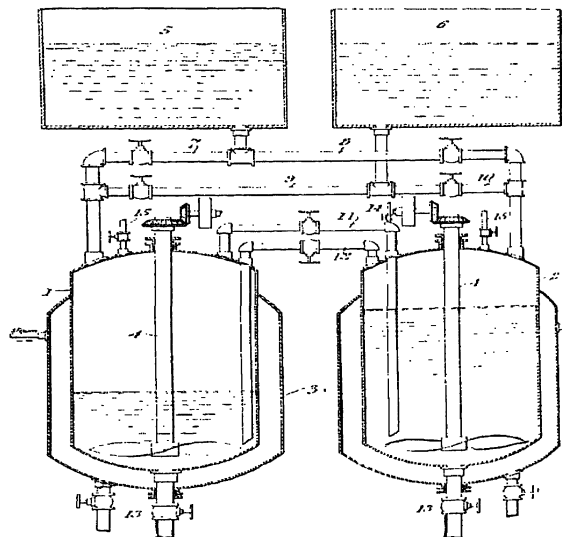
Figure 159.—Reaction vessels for making ethylene glycol from ethylene chlorhydrin. Vessel 2 contains the solutions of bicarbonate and chlorhydrin; the gas evolved passes into the cold caustic solution in vessel 1. (From the patent.)

Ethylene Glycol from Ethylene Chloride. Ethylene glycol may also be made from ethylene chloride $C_2H_4Cl_2$ in a single step.[9] The following materials in the proportions indicated are placed in a kettle with a closed, vertical extension which is jacketed, so that its temperature may be regulated.

10 parts by weight	ethylene chloride
10 parts by weight	soda ash
2 parts by weight	sodium acetate
15 parts by weight	85 per cent ethyl alcohol

The kettle is heated to 125° to 175° C. (257° to 347° F.); the pressure developed is regulated to 150 to 200 pounds by releasing some of the carbon dioxide produced. After several hours, the action is over; the sodium chloride formed is insoluble in the liquor, and may be settled out or centrifuged. The liquor consists of glycol and alcohol, and these are separated by distillation.

[9] U. S. Patent 1,402,317.

Ethylene chloride, $C_2H_4Cl_2$, has become an important substance; it is a solvent, and also a starting point for chemical syntheses. It is formed by passing ethylene gas into a cylindrical container in which a contact substance such as activated charcoal has been placed. Chlorine gas enters at the same level, and the two gases travel downward; the liquid product is trapped in a separator. $C_2H_4 + Cl_2 = C_2H_4Cl_2$. The gases may also be introduced into a body of liquid from previous batches, under a layer of water. The heat of formation of ethylene chloride is considerable (60 calories per gram-mol), and must be removed by cooling coils or a cooling jacket.

Ethylene glycol may also be obtained from glycol diacetate,[10] itself made from ethylene chloride by a procedure to be discussed presently. The glycol diacetate, a liquid, is mixed with an alcohol such as ethyl alcohol, and 2 per cent sulfuric acid, and the mixture heated in a Duriron reaction vessel. Ethyl acetate passes out and is collected, as it forms a marketable by-product. After neutralizing, the glycol is distilled from the residual liquor.

GLYCOL ESTERS

One of the earliest derivatives of ethylene glycol was the acetate ester, a substance which has good solvent properties; since then a number of other esters have been manufactured, but the ether-alcohols and the ether-esters, both to be presented in this chapter, have overshadowed the esters. The esters are important intermediate products between ethylene chloride and glycol, for example.

It may be noted that a mono-ester of a glycol is an alcohol ester, while the corresponding di-ester would have no alcohol group.

A satisfactory, inexpensive method [11] of forming ethylene glycol mono-acetate consists in placing glycol and acetic acid in a boiling kettle (copper) with a vertical extension serving for refluxing a part of the vapors evolved. The temperature is maintained around 100° C. (212° F.); the water formed during esterification is able to escape through the refluxing jacket, while glycol, acetic acid or ester are re-condensed. Any water of dilution introduced with the acetic acid will also pass out, so that it is the special merit of this method that the ester may be produced with weak acetic acid such as 25 per cent acid, a cheaper material than 99 per cent or 99.8 per cent acid. The boiling is continued until the acid is essentially all combined.

$$OH.CH_2.CH_2.OH + HOOC.CH_3 = OH.CH_2.CH_2.OOC.CH_3 + H_2O.$$
<div align="center">ethylene glycol
mono-acetate</div>
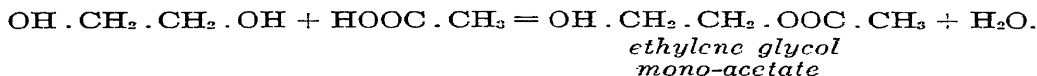
The ester is purified by distilling it; any unchanged acid passes over first, then the ester.

[10] U. S. Patent 1,454,604.
[11] U. S. Patent 1,534,752.

The diacetate is formed in just the same way, except that twice the amount of acetic acid is placed in the kettle. The reaction then is:

$$OH.CH_2.CH_2.OH + 2HOOC.CH_3 = CH_3.COO.CH_2.OOC.CH_3 + 2H_2O.$$
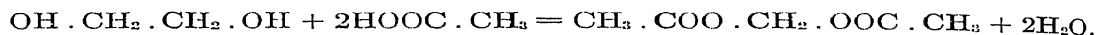
The diacetate may also be made from ethylene chloride, by heating it to 160° C. (320° F.) under pressure with sodium acetate and ethyl alcohol as a diluent.[12]

Glycol Nitrates. Ethylene glycol dinitrate is manufactured very much as nitroglycerin is, and it is used as an explosive. Its effectiveness as an explosive equals that of nitroglycerin; its great value is in the manufacture of low-freezing dynamites, as it freezes at −22.8° C. (−9° F.), while nitroglycerin freezes at + 13° C. (+ 55.4° F.). It is less sensitive to shock than nitroglycerin. Diethylene glycol may also be nitrated; the resulting dinitrate has the low freezing point of −11.3° C. (+ 11.5° F.), and is used with ethylene glycol dinitrate in the manufacture of low-freezing dynamites.

Glycol Ethers

The insistent demand for chemicals which would be good solvents for nitrocellulose stimulated the study of glycol derivatives. It was thought that the combination of the ether group with the alcohol group in a single molecule should confer superior solvent properties,[13] because the first solvent for nitrocellulose was an ether-alcohol mixture; neither of the substances alone had any solvent action. This exceptation was fully and brilliantly realized. One of the first compounds of this type was the mono-ethyl ether of ethylene glycol $OH.CH_2.CH_2.OC_2H_5$, sold under the name of Cellosolve.

A simple and efficient method for its preparation, in a single step, from inexpensive reagents, is as follows [14]: Ethylene glycol of commercial grade, di-ethyl sulfate, and caustic soda (crushed solid) in the proportions required by the reaction

$$2OH.CH_2.CH_2.OH + 2NaOH + (C_2H_5)_2SO_4 =$$
$$2OH.CH_2.CH_2.OC_2H_5 \quad Na_2SO_4 + 2H_2O$$
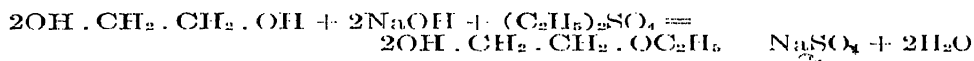
and boiled in a kettle with reflux tower for 3 hours. After that time, the liquor is vacuum distilled, leaving the inorganic salt in the still. The distillate is redistilled at atmospheric pressure and the recovery is 60 per cent or over. The product is a colorless liquid boiling at 134° C. (237° F.); it is soluble in water, glycerin, ethylene glycol, amyl acetate and butyl acetate. It is a solvent for gums, resins, and nitrocellulose; it has been proposed as an extraction agent for essential oils for flavors and perfumes. This product is the mono-ethyl ether of ethylene glycol,

[12] U. S. Patent 1,430,324.
[13] *Ind. Eng. Chem.*, **18**, 700 (1926).
[14] U. S. Patent 1,614,883.

with the ether oxygen binding the ethyl group to a carbon atom of the glycol group: $OH.CH_2.H_2C/O/C_2H_5$.

Another process [15] starts with ethylene oxide, and causes one molecule of ethyl alcohol to add itself to one molecule of the oxide

$$\begin{matrix} CH_2 \\ CH_2 \end{matrix} : O + C_2H_5OH = OH.CH_2.CH_2.OC_2H_5.$$
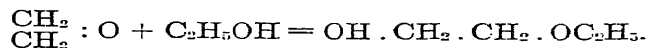
Ethylene oxide, a liquid at room temperature only when under pressure, is pumped into an autoclave into which absolute ethyl alcohol has been placed, in the proportions indicated by the reaction and a 15 per cent excess alcohol. The autoclave is then sealed and the temperature raised to 150° C. (302° F.) and kept there for 12 hours; or it may be heated to 200° C. (392° F.) and kept at that mark for 4 hours. At 150° C., the pressure rises to 250 pounds per square inch at the beginning of the reaction and toward the end falls to 125 pounds. The product is fractionally distilled to remove residual ethylene oxide and alcohol; the glycol ether passes over at around 134° C. (273° F.), leaving in the still the higher boiling reaction products such as the ethyl esters of di- and triethylene glycols which are formed to a certain extent. The yield is 70 per cent based on the alcohol reacted.

Other Glycol Derivatives. An ether-ester is formed by treating for example mono-ethyl ether of ethylene glycol with acetic acid in the same way the mono-acetate ester of ethylene glycol is prepared. Such chemicals have proved of value as solvents.

The polyglycols and mixed polyglycols are formed by heating the glycol or mixed glycols with a moderate amount of phosphoric acid, or other dehydrating agent; they are also obtained as by-products in any reaction in which two glycol molecules might suffer dehydration. Several examples of such higher glycols are given in the Table of Relation for ethylene derivatives. The reader will please note that diethylene glycol has an ether oxygen in the molecule, and triethylene glycol two: their properties are therefore rather those of ether-alcohols, and not closely resembling those of glycerin. Not only ethylene, but also propylene $CH_3CH_2.CH_2$, butylene $CH_3.CH_2.CH_2.CH_2$, and isomers, lead to glycols, each one of which gives ethers, esters, and mixed ether-esters and ether-alcohols which may have a special merit in some industrial application. For nitrocellulose and similar lacquer-forming substances, the ethylene glycol derivatives have about the right range of vapor pressure at medium and room temperatures.

Ethylene oxide is formed from ethylene chlorhydrin, by the action of an alkali stronger than sodium bicarbonate. Similar cyclic ethers of larger molecular weights are now commercial products; thus dioxan, really 1,4-dioxan

$$O \begin{matrix} .CH_2.CH_2. \\ .CH_2.CH_2. \end{matrix} O$$
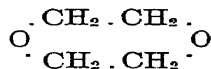
[15] U. S. Patent 1,696,874.

TABLE 54.—*Synthetic Organic Chemicals, Mainly Ethylene Derivatives.**

Name	Formula	Sp. gr. 15°/15° C.	B.P. °C. at 760 mm.	V.P. at 20° C. mm.Hg.
Acetic acid	$CH_3.COOH$	1.049	118	....
Acetic anhydride	$CH_3.CO.O.CO.CH_3$	1.082	140	....
Acetone	$CH_3.CO.CH_3$	0.7972	56.2	186.3
Dichlorethyl ether	$CH_2Cl.CH_2OCH_2.CH_2Cl$	1.230	178	0.73
Di-ethanol-amine	$(C_2H_4OH)_2NH$	1.10	271° at 150 mm.	<0.01
Diethylene glycol	$CH_2OH.CH_2OCH_2.CH_2OH$	1.1212	244.5	<0.01
Diethylene glycol ethyl ether or "Carbitol"	$CH_2OH.CH_2OCH_2.CH_2OC_2H_5$	0.9996	198	0.13
Diethylene glycol butyl ether or "Butyl Carbitol"	$CH_2OH.CH_2OCH_2CH_2OC_4H_9$	0.940	222	0.05
Dioxan	$CH_2OCH_2.CH_2OCH_2$ (ring)	1.0418	100.8	29
Ethyl alcohol (absolute)	$C_2H_5.OH$	0.789	78	44
Ethyl ether	$C_2H_5.O.C_2H_5$	0.719	34.5	425
Ethylene chlorhydrin	$CH_2OH.CH_2Cl$	1.213	128	....
Ethylene chlorhydrin 42.3 per cent	$CH_2OH.CH_2Cl$	1.0979	96	12
Ethylene diamine	$NH_2.CH_2.CH_2.NH_2$	0.902	117	....
Ethylene dichloride	$CH_2Cl.CH_2Cl$	1.266	83.5	68
Ethylene glycol	$CH_2OH.CH_2OH$	1.1176	197.2	0.09
Ethylene glycol methyl ether or "Methyl Cellosolve"	$CH_2OH.CH_2OCH_3$	0.9748	124.5	7.5
Ethylene glycol ethyl ether or "Cellosolve"	$CH_2OH.CH_2OC_2H_5$	0.9360	134.8	4.6
Ethylene glycol butyl ether or "Butyl cellosolve"	$CH_2OH.CH_2OC_4H_9$	0.9188	170.6	0.85
Ethylene glycol ethyl ether acetate or "Cellosolve acetate"	$CH_3COOCH_2.CH_2OC_2H_5$	0.976	153	1.26
Ethylene oxide	$CH_2.O.CH_2$ (ring)	0.887 at 7° C.	10.5	1020
Isopropanol 87.9 per cent	$CH_3.CHOH.CH_3$	0.8229	80.3	35
Isopropyl ether	$(CH_3)_2CH.O.CH(CH_3)_2$	0.730	67.5	158
Methanol	CH_3OH	0.7965	64.7	95
Monoethanolamine	$(C_2H_4OH)NH_2$	1.04	171° at 150 mm.	0.5
Triethanolamine	$(C_2H_4OH)_3N$	1.12	277° at 150 mm.	<0.01
Triethylene glycol	$CH_2OH(CH_2OCH_2)_2CH_2OH$	1.120	278	<0.01

* In part, from the information bulletin issued by the Carbide and Carbon Chemicals Corporation, New York.

obtained by distilling ethylene glycol with concentrated phosphoric acid, is of value as solvent.

A modified ammonia has been formed by allowing ethylene chlorhydrin to react with ammonia; triethanol amine is the best known of the three possible modifications. (For properties, *see* Table 54.) It is of great value as an emulsifier; it forms with fatty acids soaps of unusual properties, and in other ways is finding wide application in the industries.[16] In another method, ethylene oxide is allowed to react with ammonia in an autoclave. The ethanol amines are viscous, hygroscopic liquids of very mild odor; they are organic bases of mild alkalinity, and combine with free fatty acids to form soaps which have solubilities different from those of metallic soaps.

Ethylene diamine is formed by heating ethylene chloride with aqua ammonia under pressure (autoclave). A continuous process has been devised,[17] and in addition, the formation of triamine essentially prevented by using 15 mols of NH_3 to 1 of $(CH_2)_2Cl_2$.

$$Cl.CH_2.CH_2.Cl + 3NH_3 = NH_4Cl + H_2N.CH_2.CH_2.NH_2.HCl$$

Dichlor-ethyl ether is formed by the removal of a molecule of water from two molecules of ethylene chlorhydrin.

A new solvent which does belong among glycol derivatives but which is of synthetic origin has been developed at Purdue University: it is 1,3-dichlor-2-methyl propane, a liquid. It has excellent solvent properties for grease, and is non-inflammable, so that it is expected that it will be a great success in the dry cleaning trade.

Ethylene reacts with steam at 400° to 500° C. and 25 to 200 atmospheres in pressure, in the presence of a dehydrating catalyst such as thoria, or phosphoric acid deposited on charcoal,[18] to form ethyl alcohol.

By means of Table 54, some additional information regarding the numerous ethylene and other olefin derivatives is given.

SYNTHETIC METHANOL

The large scale synthesis of methanol CH_3OH, the same substance as wood alcohol, from carbon monoxide and hydrogen with the aid of a contact substance was brought to the notice of the American public with dramatic suddenness. A few years after the war (in 1923), with the economic world resuming its normal pace, there were delivered in New York harbor thousands of gallons of synthetic methanol, to be sold, duty paid, for 40 cents a gallon, a price about half that charged for methanol from wood at that time. Readjustments have been made since then, but the advantage remains with the synthetic product. Not only are the raw materials it requires cheap and abundant, not only have the technical problems of low, medium, and now, high pressure catalysis been solved,

[16] *See* gas purification, Chapter 14.
[17] U. S. Patent 1,832,534.
[18] Brit. Patent 208,859, Jan. 1928.

but the methanol reaction serves to utilize by-products which otherwise would be wasted, and it has been applied to remove an undesirable component of a gas mixture (CO in H_2 for ammonia). For several years, methanol from wood maintained an artificial advantage, because the prohibition law read that "wood alcohol, a product from wood," must be used in the chief denaturing formula; in 1929, this advantage was lost. Alcohol from wood must now compete with synthetic methanol for regular commercial and industrial uses.
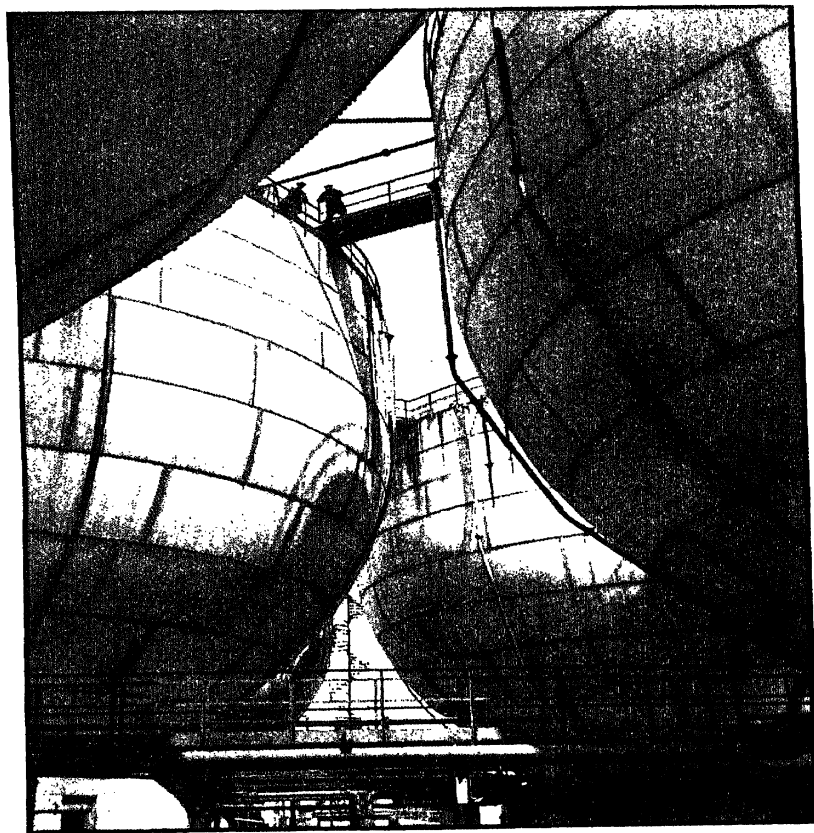
FIGURE 160.—Storage tanks for synthetic organic chemicals such as methanol, Leuna Works, I. G. Farbenindustrie, Germany. (Bourke-White Photo, Pictures, Inc., N. Y.)

Since 1923, plants synthesizing methanol have been erected in the United States, and have been most successfully operated. The production in 1931 was 7,766,592 gallons; in 1935, it was 120,750,861 pounds (4 cents a pound); this would be about 18.3 million gallons. For comparison, the production of wood alcohol was 1.95 million gallons, 1935.

When a mixture of carbon monoxide and hydrogen, such as is contained in water gas, is passed at atmospheric pressure over nickel held at a temperature of 380° C. (716° F.) there is formed methane and car-

bon dioxide. $2CO + 2H_2 = CH_4 + CO_2$. With the volume adjusted so that to 1 volume of carbon monoxide there are 3 volumes of hydrogen, the reaction goes practically to completion at the temperature of 230° to 250° C. (446° to 482° F.).

With high pressures, and zinc oxide as catalyst, the reaction takes another course; methanol is produced. Since the earliest study [19] of this reaction, an improved catalyst, namely, zinc oxide with 10 per cent chromium oxide,[20] has been proposed and used. The reaction $CO + 2H_2 = CH_3OH$ takes place with fewest side-reactions if the ratio of monoxide to hydrogen is as 1 is to 2.2. The conversion is 20 to 25 per cent, depending not only on the repression of side reactions, but also on the activity of the catalyst and on the space velocity. For a given catalytic activity, the greater the space velocity, the lower the conversion figure.

Since the action $CO + 2H_2 = CH_3OH$ is exothermic (24 Calories at 350° C. or 662° F.), the amount of methanol in an equilibrium mixture of the three gases will be decreased as the temperature is raised; the reaction is favored by relatively low temperatures. Also, as the pressure is increased the amount of methanol rises, for the reaction involves a reduction in volumes, from 3 to 1, for the portion of the gases which reacts. At temperatures above 250° C. (482° F.), less than 0.1 per cent methanol can be formed,[21] at atmospheric pressure, while at 300° C. (572° F.) and 300 atmospheres, for example, 45 per cent methanol formation is possible. Table 55 gives the percentage of methanol at equilibrium; in commercial practice, the long time required for equilibrium to be attained cannot be provided, and therefore a lower conversion must be accepted.

TABLE 55.—*Percentage Methanol at Equilibrium Ratio $H_2/CO = 2$.*

Temp. °C.	Pressure (atm. absolute)						
	1	10	50	100	300	600	1000
200	0.32	28.10	58.40	71.95	85.62	90.70	93.40
300	...	0.25	5.47	15.62	43.05	59.80	69.80
350	...	0.04	1.02	3.69	19.51	37.11	50.46
440	...	...	0.20	0.85	6.35	17.30	29.80
500	...	...	...	0.07	0.61	2.34	5.80
600	...	...	...	...	0.09	0.37	1.02

The catalyst is so chosen that it hastens the reaction, and does not favor the formation of other products. The composition of the catalyst and the method of preparation, as well as the conditions of temperature and pressure which are found to be most advantageous, must be set. Construction and procedure must take into account the necessity of dissipation of heat from the granules of catalyst, as well as the need of preheating the incoming gases to reaction temperature.

[19] The original catalyst was 90 parts copper oxide with 10 parts zinc oxide, used by Patard; for the early history of the methanol developments, see *Ind. Eng. Chem.*, **17**, 430 (1925); also Brit. Patent 229,715 to a Badische Anilin und Soda Fabrik correspondent, reproduced in *Ind. Eng. Chem.*, **17**, 981 (1925). *See also* p. 859, same journal and volume.

[20] The Mittasch patent, U. S. Patent 1,558,559.

[21] U. S. Patent 1,844,857.

The gas mixture may be 70 per cent hydrogen and 30 per cent carbon monoxide, or 80 per cent hydrogen and 20 per cent carbon monoxide; it may contain small or large volumes of inert gas such as nitrogen, without harm,[22] but in the American plants, the nitrogen is either low or absent. The gas mixture of the proper composition is compressed, and the pressure is chosen as low as 50 and as high as 1000 atmospheres in different plants. It then travels through the converter chamber of suitable material as to strength, at a rate which permits a good conversion. Table 56 will indicate the conversion which may be expected for various space velocities.

The gas must be free from sulfur, arsenic, and even carbonyls; these latter might introduce iron, and this metal as well as nickel and cobalt must be avoided, for they catalyze the formation of methane.

TABLE 56.—*Methanol Conversion at 400° C. (752° F.).**

Gas mixture	Space velocity	Pressure Atm.	Conversion Per cent
$CO + 5H_2$	500	150	22.5
$CO + 2.7H_2$	625	204	26
$CO + 2H_2$	3000	180	19.5
$CO + 2H_2$	7500	180	16.8

* *Ind. Eng. Chem.*, **20**, 1111 (1928).

The converter is preceded by an exchanger in which the outgoing gases give up much of their heat to the incoming ones. After the gas is compressed and heated, it must come in contact only with copper or aluminum surfaces; the converter is of nickel steel, copper-lined. On cooling, the outgoing gas suffers liquefaction of the methanol formed; this is removed in a separator, and the unconverted gas returned to the compressors. The conversion is around 20 per cent. The critical temperature for methanol is 240° C. (464° F.), the critical pressure 78.7 atmospheres; a slight cooling of the converted gas is therefore sufficient to allow liquefaction. The synthesis is exothermic, furnishing enough heat to run the process without outside heat source except when starting.

The methanol synthesis has been employed to rid the hydrogen-nitrogen gas mixture for the direct ammonia synthesis from small amounts of carbon monoxide, as already stated in the introduction to this section. In such cases there is present a considerable excess of hydrogen; conversely, the percentage of carbon monoxide is low. It is necessary to have a highly active catalyst, so that this small amount of carbon monoxide might be completely transformed into methanol. Such a catalyst is obtained[23] by melting together pure copper oxide and any oxide of chromium, titanium, molybdenum, zinc, or manganese, breaking up the resulting melt into fragments, and reducing these in hydrogen at 250° to 350° C. (482° to 662° F.). The copper oxide suffers reduction, leaving the metal; the other oxide is unreduced. The granules produced by

[22] In fact, it is recommended in Brit. Patent 306,512 (1928) that an inert gas be added and circulated, in order to dissipate the heat.
[23] U. S. Patents 1,844,857 and 1,844,129.

this method are hard, highly porous, and very reactive at relatively low temperatures.

The efficiency of this catalyst is high, which means that the percentage of methanol (as gas) in the gas mixture leaving the reaction bomb is high for each unit volume of catalyst, at given pressure and temperature, compared with other masses. The metallic copper tends to dissipate the heat of reaction and thus favors formation of methanol.

A catalyst so produced will cause as little as 3 per cent carbon monoxide in the hydrogen gas to react. Pressures of 200 to 300 atmospheres are suitable, but at 1000 atmospheres the reaction proceeds smoothly.

The methanol formed is removed by cooling the compressed gas to between 0° and 20° C. (32° and 68° F.), when it liquefies; the residual gases are returned to the high pressure system and sent to the ammonia converters. Zinc oxide is avoided in the methanol converters, because it may allow a trace of metallic zinc to form, which the gas would carry to the iron catalyst, poisoning it.

In all catalytic processes, the preparation of the catalyst is an important major operation. For the methanol catalyst, the following preparation [24] will serve as an example: Zinc oxide is stirred into a chromium nitrate solution, and the whole evaporated to dryness; the heating is continued until the nitrate is converted into oxide. The product is mixed with dextrin solution containing zinc chloride, then dried and granulated. The catalyst is packed in the converter in granule form.

On distilling the synthetic methanol it is found to contain a higher boiling fraction, consisting of higher alcohols. An explanation for their formation from methanol has been offered.[25]

The term "methanol synthesis" has come to stand for a series of syntheses from the oxides of carbon and hydrogen. The six main classes of compounds which are obtained are shown below:

$$CO + H_2 \text{------} CH_2O \text{------} CH_3OH \text{------} \begin{cases} \text{------Alcohols} \\ \text{------Acids} \\ \text{------Ethers and esters} \\ \text{------Aldehydes and ketones} \\ \text{------Hydrocarbons} \\ \text{------Cyclic compounds} \end{cases}$$
intermediate
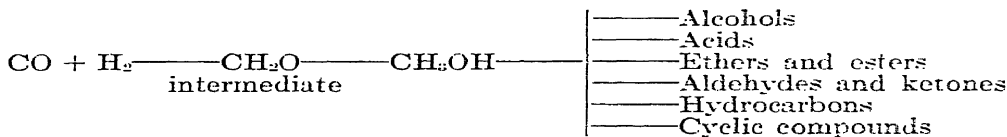
The reaction achieved depends upon or is governed by the nature of the catalyst; with zinc oxide, as has been shown, the main reaction, the production of methanol, is favored, and the side reactions are repressed. By the use of cobalt metal with chromium oxide, for example, the formation of hydrocarbons is favored. The desired side reaction is produced almost to the exclusion of all the others by the proper choice of catalyst, and especially by the use of mixed catalysts.

Methanol is an antifreeze for the automobile, a solvent for lacquer manufacturers, the raw material for most of the formaldehyde made,

[24] Brit. Patent 272,864 (1926).
[25] Higher alcohols formed from carbon monoxide and hydrogen, by G. D. Graves, *Ind. Eng. Chem.*, **23**, 1381 (1931).

for methyl chloride, and to a minor degree, a denaturant for tax-free alcohol.

The total for non-coal tar synthetic organic chemicals produced in the United States in 1935 was 1,591,895,576 pounds, valued at $1,750,000,000.

GENERAL STATEMENT REGARDING THE CHOICE OF CATALYST

Many of the reactions discussed in this chapter are catalytic in nature. Elsewhere in the book a number of others will be found in their proper place; some of these are indicated in Table 57, "Some Catalytic Reactions of Industrial Importance." A few general remarks regarding catalysts and their function will supplement the information given elsewhere, and clarify some of the underlying general principles.

The original discoveries, by Sabatier, consisted mainly of hydrogenation of hydrocarbons in the vapor phase, in contact with metallic nickel especially, at ordinary pressures. To-day, nickel and other metals of the same type, cobalt, iron, copper and platinum, are still used for hydrogenation, for example, that of vegetable oils for the production of edible and non-edible vegetable fats.

There are two ways in which a catalyst may lose its efficiency: one is by heat, the second by poisoning. Nickel is sensitive to impurities, so much so that the hydrogen used must be absolutely pure, and the material to be hydrogenated must not contain any elements which might affect the nickel. The same applies to the other four metals listed.

In the hydrogenation of mineral oil, in hydrofining, it is out of the question to use such a delicate material as nickel, or any metal sensitive to sulfur. For ·tely, a number of oxides have been found to have excellent hydrogen functions, and at the same time are resistant to impurities, and, p₁, ·ly chosen, also to the deactivating effect of continued heating. Such hydrogenating oxides are molybdenum, tungsten, manganese, vanadium, and chromium oxides, with alumina, magnesia, zinc oxide, and potassium carbonate as promoting agents (used in small amounts).

For hydration and dehydration in the vapor phase, the oxides which are most efficient and durable are thoria, alumina, tungstic oxide, silica, titania, and zirconia; also those of the alkalies and alkaline earths.

The hydration of acetylene takes place in the liquid phase, and the most satisfactory material is mercurous sulfate.

For oxidation processes the metals of the platinum series, as well as oxides and salts of metals which can exist in two or more states of oxidation, are the most important catalysts.

GENERAL REMARKS ON CATALYSIS

A distinction is made between atmospheric or low pressure catalysis and high pressure catalysis. As one would expect, the first work of Sabatier was at low pressures, and only subsequently was the field of high pressure catalysis revealed. Different materials differently con-

TABLE 57.—*Some Catalytic Reactions of Industrial Importance.*

Reaction	Catalyst	Temperature ° C.	Pressure Atm.	Heat effect	Cal.
$2CO + 2H_2 = CH_4 + CO_2$	Ni	380	1	exothermic	60 *
$CO + 3H_2 = CH_4 + H_2O$	Ni	240	1	exothermic	
$CO + H_2O = CO_2 + H_2$	Fe	500	1	exothermic	10 *
$CO_2 + 4H_2 = CH_4 + 2H_2O$					
$CO_2 + CH_4 = 2CO + 2H_2$	$Ni + Al_2O_3$	900	1		
$CO + H_2 = synthin$	$Co + Cr_2O_3$	270	1		
$CO + 2H_2 = CH_3OH$	$ZnO + 10\% \; Cr_2O_3$ {lumps or granules}	350	200	exothermic	24 *
$CO + 2H_2 = CH_3OH$	Cu	350	200	exothermic	
$CO_2 + 3H_2 = CH_3OH + H_2O$	$ZnO + 10\% \; Cr_2O_3$	350	200	exothermic	14 *
$CO + H_2 = synthol$	$Fe + K_2CO_3$	400–450	100		
$Coal + H_2$	none (Bergius)	400	100		
$Coal + H_2$	Mo_2O_3 on Al_2O_3				
Min. oils $+ H_2$	Mo_2O_3 on Al_2O_3		245	exothermic	
$C_2H_2 + H_2O = CH_3CHO$	Hg_2SO_4	68	1	exothermic	28.14 *
$CH_3CHO + \frac{1}{2}O_2 = CH_3COOH$	$MnSO_4$	25	2–3	exothermic	56.6 *
$N_2 + 3H_2 = 2NH_3$	Fe greed with double promoter (American)	475	300	exothermic	11.89 †
$4NH_3 + 5O_2 = 4NO + 6H_2O$	Pt gauze	1025	1–3	exothermic	214.2 *
$SO_2 + \frac{1}{2}O_2 = SO_3$	Pt; or V_2O_5	500	1	exothermic	22.6 *

* Calories (large) evolved for the reaction as written; † for 17 grams of ammonia. Exothermic means with evolution of sensible heat to the outside; the chemical system involved loses the corresponding amount of heat, and is therefore written with a minus sign in thermodynamics.

structed had to be devised to withstand the high pressures at the elevated temperatures, and the accelerated chemical activities on container walls. A vast amount of information on the compressibility of gases and gas mixtures, on the flow of compressed gases through narrow bores, on chemical equilibria, had to be obtained, before the present state of development was reached. The application of catalytic reactions to the industrial processes has only begun.

It was formerly held that a catalytic agent accelerated a reaction which was slow, but could take place of itself. It is well to modify this in two respects, and to say: A catalyst hastens a slow, or even very slow chemical change, which, however, must be thermodynamically possible, and, when several products are obtainable, the catalyst is capable of directing the reaction.

Any substance which accelerates a reaction is a catalyst; it may be a dissolved substance in a liquid in which gases must in their turn dissolve, such as the violet acid in the sulfuric acid-nitric oxide chambers, or the hydrogen chloride and tin compounds in some of the hydrogenations of tars and coal to give motor fuels. The contact catalyst is frequently a solid, which is exposed to the gases, vapors, or to the liquid in which the reaction is to take place; the solid may be in lump form, or powder; it may be by itself, or it may be supported on a "carrier," itself inert.

The activity of, let us say, a metal surface in the case of hydrogenation resides at the surface of the metal. A comparatively small number of the surface atoms project into space, and are unbalanced with respect to their chemical affinities or valence. (*See* Fig. 161.) These projecting
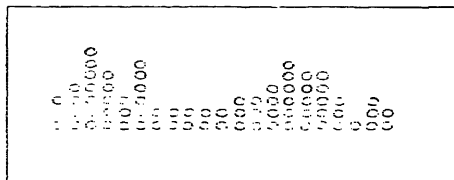
FIGURE 161.—The surface of metallic nickel, greatly enlarged to show the catalytically active centers formed by protruding atoms. (After Taylor.)

atoms form intermediate compounds, or complexes with the hydrogen; the forces involved are not distinguishable from the common chemical forces. If such an active center or a near-by one can also attract the second reactant, such as carbon monoxide, similarly distorting its normal structure, the two substances can meet while in the active state, and readily form a new grouping. Questions of adsorption are of the first importance; in some cases adsorption stops the process. For example, 3 per cent carbon monoxide in hydrogen will retard the ammonia formation, because the monoxide is adsorbed by the surface, thus preventing the approach of the hydrogen. The monoxide is then spoken of as a poison. Promoters in this theory would be substances which distort the crystal lattice in the catalyst still more than it normally is; in other cases, these

promoters would be able to form the temporary complexes with the reactants, necessary for the rapid change.

The rôle of temperature will be a compromise between two or more effects; it must not be so high that the adsorbed atoms and molecules are driven off so fast that no or little reaction can take place; yet it must be high enough so that the activation of the reactant molecules is a maximum, and that very little additional force at the contact surface will suffice to form the adsorption complex.[26]

A figure in constant use in catalytic reaction studies is the space-velocity, by which is meant the volume of reacting gases passing over one liter of catalytic mass per hour. The volume in question is the volume of the exit gases, calculated to normal conditions of temperature and pressure, while the volume of catalytic mass is the volume occupied by the mass as spread out or packed in the reaction vessel.

The greater number of catalytic reactions presented in these chapters are heterogeneous, that is, involve two or more phases, such as solid and gas, or solid, liquid and gas. A homogeneous catalytic reaction would be the inversion of sucrose in solution by a dissolved acid. A heterogeneous catalytic reaction involving three phases is the hydrogenation of edible oils, in which hydrogen (gas), the oil (liquid) and the contact substance, nickel (solid), participate.

HYDROGENATION AND OXIDATION OF HYDROCARBONS

Among the most important catalytic reactions are those which incorporate into a hydrocarbon from natural sources, such as naphthalene or benzene, hydrogen or oxygen. The solid naphthalene, on gaining 4 hydrogen molecules, turns into the liquid tetralin; on oxidation, the liquid benzene turns into the solid maleic acid. A great variety of products have been obtained, and they might indeed, as suggested in the introduction to this chapter, be called semi-synthetics. It is, however, customary not to make the distinction, but to speak of them as synthetics.

Tetralin. Naphthalene vapors mixed with hydrogen (very pure) are passed over nickel held at 150° to 200° C. (302° to 392° F.), at ordinary pressure; tetralin is formed : $C_{10}H_8 + 2H_2 = C_{10}H_{12}$. Naphthalene melts at 218° C. (424.4° F.); tetralin boils at 205° to 207° C. (401° to 405° F.). This is a hydrogenation in the vapor phase.

Naphthalene may be melted in an autoclave with stirrer and nickel suspended in it, very much as is done for the hydrogenation of edible oils; at 140° to 160° C. (284° to 320° F.) hydrogen is forced in under a pressure of 30 atmospheres. Tetralin is formed. On long-continued hydrogenation, decalin is obtained, largely. $C_{10}H_8 + 5H_2 = C_{10}H_{18}$. The latter substance is more expensive to prepare, and has no great advantage over tetralin, so that its industrial importance is small.

[26] For the theory of the mechanism of catalytic processes, see "Eighth report of the committee on contact catalysis," J. C. W. Frazer, *J. Phys. Chem.*, **34**, 2155 (1930).

Benzene vapors with hydrogen over nickel at 140° C. (284° F.) give cyclohexane $C_6H_6 + 3H_2 = C_6H_{12}$, a liquid. Expressed graphically:

$$
\begin{array}{c}
+ 3H_2 =
\end{array}
\qquad
\begin{array}{c}
H_2 \\
H_2 \qquad H_2 \\
H_2 \qquad H_2 \\
H_2
\end{array}
$$
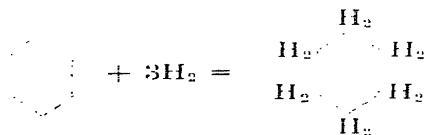
Phenol by a similar procedure gives cyclohexanol.

Phthalic Anhydride. By controlling the oxidation by air of naphthalene, a good yield of phthalic anhydride may be obtained; the catalyst is vanadium pentoxide, at an elevated temperature. This was one of the earliest triumphs of catalytic chemistry outside of the sulfuric acid synthesis. By controlling is meant arresting it at a certain stage, for should it be allowed to proceed unchecked, only carbon dioxide and water would be the products.

In the most successful of the commercial installations,[27] air and naphthalene vapors from boiling naphthalene are thoroughly mixed in a hot mixing chamber, and passed over the catalyst in numerous square tubes,
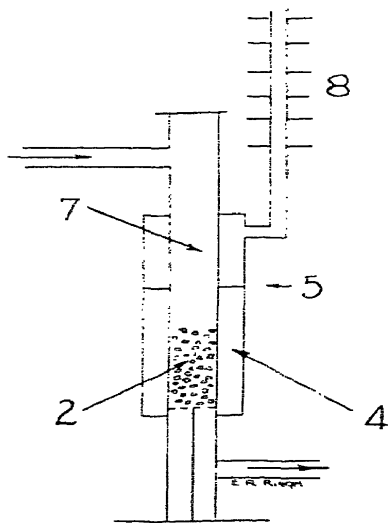
FIGURE 162.—Air-hydrocarbon oxidation. Single tube, with catalyst mass 2; level of mercury in the jacket 5; total condenser for the mercury 8; preheating part of reaction tube 7. In the full size installation, a nest of tubes is used.

kept at about 357° C. (674.6° F.), in a downward direction. Figure 162 will illustrate the disposition. Around the tubes a small body of liquid mercury is gently boiling. The converter consists of a nest of such tubes set in mercury, the whole surrounded by an outside jacket; the latter carries a vertical tube with fins which acts as an efficient condenser for the mercury. As the hydrocarbon and air react (on the surface of the vana-

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[27] U. S. Patent 1,374,720; for the basic patent of Gibbs, see U. S. Patent 1,285,117. See also U. S. Patent, 1,444,068. In 1930, the Gibbs patent was cancelled, and U. S. Patents 1,787,417 and 1,787,416 were issued to Alfred Wohl, for the same process. These were attacked in court by the government, but in 1934, the Wohl patents were upheld and declared valid (see Chapter 40).

dium pentoxide), much heat is evolved; it passes through the wall of the square tube to the mercury, which consumes it by vaporizing. In that way, the temperature is maintained near the boiling point of mercury, 357° C. (674.6° F.). The catalyst tube is empty for its upper half, and this part becomes the preheater for the incoming gases, which are already at an elevated temperature. The main reaction is

naphthalene
(white solid)

phthalic anhydride
(white solid)
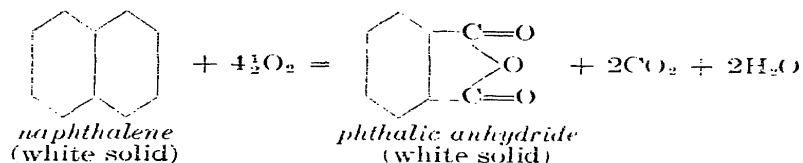
To a certain extent, benzoic acid C_6H_5 . $COOH$ and naphthaquinone,

are formed, and are collected with the anhydride, while the gases pass out. A 72 per cent recovery of phthalic anhydride is feasible; it is isolated by sublimation, and is put on the market in the form of flakes and "crusts."

In the original installations, the catalyst was made by dipping asbestos fibers in ammonium vanadate, and activated by passing hot air through it; instead of asbestos, pumice may be used. The square tubes as catalysts carriers are used because the ratio of surface to content is greater for a square tube than for a round one of same height and same cubical content. It should be noted that this oxidation is performed at atmospheric pressure. The temperature may be varied by operating under slightly higher pressures. Instead of mercury, liquid sulfur may be used.[28]

The yearly production of phthalic anhydride by catalytic oxidation in the United States is over 23 million pounds (1935).

Maleic Acid. In the same apparatus serving for phthalic anhydride production, maleic acid is formed by the oxidation of benzene at a slightly higher temperature. A recovery of 60 per cent is considered good.

maleic acid
(white solid)

maleic acid

maleic anhydride
(white solid)
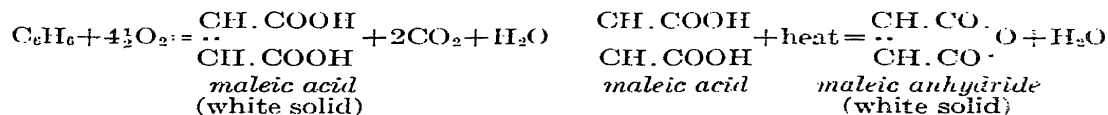
Maleic acid may be hydrogenated to succinic acid, or hydrated to malic acid; the latter is a substitute for citric acid in beverages. The esters formed from these acids in the standard way are valuable for their odor, and solvent properties.

[28] U. S. Patent 1,547,167.

$$CH.COOH \qquad CH_2.COOH \qquad\qquad CH.COOH \qquad CH(OH).COOH$$
$$CH.COOH + H_2 = CH_2.COOH \qquad CH.COOH - H_2O = CH_2.COOH$$

succinic acid   *malic acid*
(white solid)   (white solid)
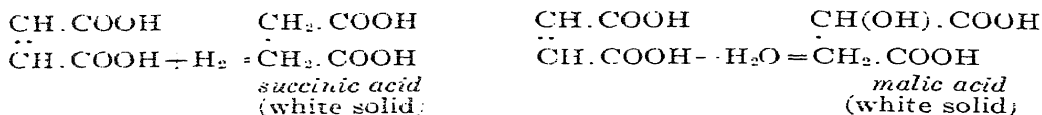
Purification by Catalysis. The best available anthracene of commerce contains 30 to 50 per cent anthracene $C_{14}H_{10}$; the chief impurities are carbazol $C_{12}H_9N$, and phenanthrene $C_{14}H_{10}$. It has been found possible to effect a purification by catalysis. The crude material is mixed in vapor form with air (1 to 35) by spraying the melted crude into hot air; the mixed gases are passed over a properly chosen catalyst at 350° C. (662° F.). The carbazol is destroyed, while practically all of the anthracene and phenanthrene are recovered unchanged. The phenanthrene may now be isolated by the use of a solvent, leaving a 90 to 99 per cent anthracene. A catalyst which favors the total combustion of carbazol and at the same time leaves the anthracene unaffected is made by suspending titanium oxide TiO_2 in a water solution containing 12 parts of potassium hydroxide, cyanide or nitrate, either singly or mixed; this suspension is coated on pumice broken to pea size, and dried. A number of other formulas are available.[29]

A high-grade anthracene is also obtained by dissolving crude anthracene in furfural, and crystallizing.[29]

Related reactions are shown in Table 58.

TABLE 58.—*Hydrogenation and Oxidation of Natural Organic Compounds.*

Compound	Catalyst	Temp. °C.	Pressure Atm.	Product
Naphthalene + 2H$_2$	Ni	150–200	1	tetralin
Benzene + 3H$_2$	Ni	150–160	1	cyclohexane
Phenol + 3H$_2$	Ni		1	cyclohexanol
Benzene + 4½O$_2$	V$_2$O$_5$	400–440	1	maleic acid
Naphthalene + 4½O$_2$	V$_2$O$_5$	350–400	1	phthalic anhydride
Toluene + 1½O$_2$	MoO$_3$; UO$_2$	400	1	benzoic acid
Anthracene + 1½O$_2$	V$_2$O$_5$	400	1	anthraquinone

OTHER PATENTS

U. S. Patent 1,598,560, on the absorption of ethylene in sulfuric acid, then with water to form ethyl alcohol; 1,599,119, ethylene and sulfuric acid to make neutral ethyl sulfate; 1,574,796, on ethyl sulfuric acid and ethyl sulfate from ethylene and sulfuric acid, catalyzed by ferrous or cuprous salts; 1,460,545, production of ethylene from ethane in natural gas; 1,402,336, production of ethylene from ethyl alcohol; 1,779,710, ethylene glycol ester of abietic acid; 1,569,775, on the absence of exposed iron in methanol synthesis, and a chromium oxide-manganese oxide catalyst; 1,738,989, on methanol synthesis; 1,824,896, on formaldehyde formation followed at once by hydrogenation with the aid of a second catalyst; 1,861,841, on dehydrating aqueous acetic acid with carbon tetrachloride; 1,875,273, production of methyl alcohol by passing gaseous mixture of hydrogen and carbon monoxide in contact with a hot catalyst mass comprising 50 per cent by weight of reduced copper, 300° to 400° C. and 5 to 300 atmospheres pressure; 1,961,736-7, forming acetic acid from methanol and carbon monoxide. J. C. Carlin and N. W. Krase; 2,031,475, oxidizing catalysts, to J. C. W. Frazer; 2,040,233, preparing contact catalysts; 1,925,602, on a stabilized solvent for metal degreasing; and 1,907,875, on an apparatus for that purpose.

[29] *Ind. Eng. Chem.*, **20**, 1330 (1928).

PROBLEMS

1. The manufacture of ethylene glycol consists of treating ethylene chlorhydrin with a solution of sodium bicarbonate. The chemical equation is given in the text. The chlorhydrin is made by the action of ethylene on hypochlorous acid. The hypochlorous acid is liberated at the moment it is to react by the action of chlorine gas on a solution of sodium hypochlorite. This substance in turn is made by the action of chlorine on a cold solution of caustic soda.

The chemical reactions are given in the text.

(a) Assuming the yields to be 100 per cent. find how much chlorhydrin was required to make 1 ton of ethylene glycol; and how much hypochlorous acid and ethylene to make the required ethylene chlorhydrin; how much sodium hypochlorite to obtain the necessary hypochlorous acid; how much chlorine to produce the sodium hypochlorite, and which second amount to liberate the free hypochlorous acid.

(b) Let the reaction for the formation of the glycol from the chlorhydrin be realized to the extent of 90 per cent, and the one for the formation of chlorhydrin from methylene and hypochlorous acid also to the extent of 90 per cent; what will be the amount of each of the items listed in (a)?

(c) Express the required amount of ethylene in cubic feet at 62° F. and 1 atmosphere's pressure; the weight for one cubic foot is 0.0738 pound.

2. The formula for the heat of reaction for the formation of methanol in gas form from carbon monoxide and hydrogen is

$$\triangle H = -18{,}050 - 19.54T + .01586T^2.$$

It applies to any temperature; the heat value is found by substituting for T the temperature of reaction in absolute degrees (or degrees Kelvin).

This expression is derived from the free energy expression

$$\triangle F = -18{,}050 + 45.00T \cdot \log_{10}T - .01586T^2 - 69.4T.$$

The change in free energy for a reaction is of more importance and influence than the heat effect.

The exact value for the heat of reaction in the table is $\triangle H_{a} = -24.059$ gram-calories or -24.059 Calories. Check this value, and find the heat effect for 400° C., 300° C., and 325° C. Compare the results. In every case, it is for how many grams of methanol?

3. The reaction for making methanol is $2H_2 + CO = CH_3OH$. In order to make 100 gallons of methanol 100 per cent pure, how much hydrogen by weight will be required; how much by volume at 0° C. and 1 atm.? The reaction is made to take place at 300° C. and 1000 atm., so that the gases entering the catalytic chamber are put under that pressure and raised to that temperature. What will be the volume of the entering gases which actually do react?

But the conversion is 25 per cent; what is the weight and volume of the gases sent into the converter?

The catalytic volume is 10 liters; with the outgoing methanol assumed to remain gaseous. and the 100 gallons to be obtained in a period of 10 hours, what is the space velocity?

Calculate the volume of the compressed gases in two ways. first. according to the gas laws; second, with the use of the compressibility coefficients:

Temp. ° C.	Pressure Atm.	Hydrogen	Carbon monoxide	Methanol
0	1	1	1	1
300	1000	2.8157	3.3203	3.3

(*Compare* problems in Chapter 6.)

4. Chlorhydrin, $OH \cdot CH_2 \cdot CH_2 \cdot Cl$, reacts with ammonia, NH_3, to form three amines,

$$\text{Monoethanolamine } (C_2H_4OH)NH_2$$
$$\text{Diethanolamine } (C_2H_4OH)_2NH$$
$$\text{Triethanolamine } (C_2H_4OH)_3N$$

These in turn are capable of reacting with acids such as stearic acid, $C_{17}H_{35}COOH$, to form soaps which are excellent emulsifying agents.

(1) Assuming commercial triethanolamine to contain 17.5 per cent DEA. and 5.0 per cent MEA., what is the theoretical yield from 1000 lbs. of chlorhydrin?

(2) What is the combining weight of the commercial TEA.?

(3) What weight of NH_3 is required for making the TEA. in (2)?

(4) What weight of stearic acid will combine with the commercial TEA. formed?

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Chapter 26

Dye Application*

In the application of dyes, two main factors have to be observed: the character of the fiber, and the properties of the dyestuff.

The character of the fiber: Cotton consists of pure cellulose: it has very weak properties, either acid or basic. Silk and wool in contrast to cotton have pronounced acid and basic properties. Consequently dyestuffs with pronounced acid or basic properties can be applied directly to wool and silk; to cotton only special classes of dyes, among others the benzidine group, are direct dyes, and are used in the form of the sodium salt. In addition, coloring matter may be fastened onto cotton in a roundabout way, by means of an intermediate compound, as in mordanting, or by building the dye in stages on the fiber.

The properties of the dyestuffs, whether acid or basic, soluble or insoluble, reducible or not, must be considered in their application; various classes of dyes require different methods.

The Character of the Fiber

Cotton. Cold concentrated sulfuric acid dissolves cotton, and on diluting with water, dextrin is precipitated. Warm dilute sulfuric acid forms hydrocellulose (hydrated cellulose) and the fibers swell; in the cold, diluted mineral acids have no action. Organic acids at room temperature have no action: at higher temperatures, the strength of the fiber is weakened. Diluted caustic, or milk of lime boiled with cotton without access of air, have no action, but in presence of air, there is formed oxycellulose.

Concentrated alkali causes the cotton filament to swell and the walls of the fiber to become cylindrical, resembling tiny glass rods. If the caustic treatment is performed while the cotton is under tension, so that the fiber cannot shrink lengthwise, the cotton develops a silk-like lustre. The process is called mercerization of cotton. The affinity of the mercerized thread for dye is much greater than the affinity of the untreated cotton, due to the oxycellulose which has been formed.

Silk. While cotton consists of a single substance, cellulose, silk consists of two: the fibrous substance, fibroin, and the silk gum, sericin. The silk gum covers the fiber: it is soluble in water and soap and can be rapidly removed by boiling, while the fibroin is insoluble. The silk threads of commerce are fibroin; and it is to this part of the original substance that the following remarks apply.

*In collaboration with Robert Kuoch, Ph.D. (Basel), Consulting Chemist for Dyes, of Buffalo, N. Y.

Concentrated mineral acids destroy silk; diluted acids are readily absorbed by silk; wool is acted on in the same way. Hot caustic soda will dissolve silk completely, but not so fast as wool.

Tin, aluminum, and iron salts are adsorbed by silk as well as by wool, with the formation of a metallic hydrate or an insoluble basic salt.

Affinity of silk to coloring matter is in general lower than that of wool; for instance, acid colors on silk are not as fast to washing as when applied to wool.

Wool. Diluted mineral acid does not affect wool, except that the acid is retained by the fiber with great tenacity; it cannot be removed by boiling with water. This is well shown as follows: Wool which has been treated with dilute sulfuric acid and then washed with boiling water several times until the water shows a neutral reaction, may be dyed in a neutral bath with a dye which ordinarily is applied in an acid bath.

Wool is readily attacked by alkali; the higher the temperature, the more ready the attack.

This fiber behaves toward dye in different ways according to its origin, so that it is essential to obtain the wool from the same source, or be ready to make preliminary dyeings; but in all cases its affinity for dye is greater than that of silk, as was stated in the previous division. It will be remembered, too, that both wool and silk have a far greater affinity for dye than cotton. Wool has pronounced acid and basic properties; it may be considered an amino acid. It is classed as a protein substance.

Aluminum sulfate, ferrous sulfate, chrome alum, and other salts with acid properties are adsorbed by wool readily; neutral salts are not adsorbed. The application of salts to wool is called mordanting; although important, it is less so than the mordanting of cotton.

Artificial Silk. In this new fiber, a distinction must be made between viscose silk, or rayon, and the cuprammonium silk, on the one hand, and acetate silk, on the other. The first two are essentially cellulose, and behave like cotton; they may be dyed in the main by means of the cotton dyes. Acetate silk is cellulose acetate, and has different properties; its affinity for dyes is distinct from the affinity cotton shows. Special dyes [1] have been developed, among others, which are colloidally dispersed amidoazo intermediates. The material is adsorbed by the fiber and is developed as described under Developed Dyes. Acetate silk is attacked by caustic soda, a hydroxyl group replacing the acetyl group. This may be turned to advantage by allowing only a slight attack and then applying dyestuffs which would not be received were the hydroxyl groups not present.

THE PROPERTIES OF DYESTUFFS

Dyestuffs are chemical compounds which have the property when in solution to color permanently, with or without the use of auxiliary

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[1] *Chemical News*, **128**, 19 (1924), also a number of articles in volumes 14 and 15, of the *American Dyestuff Reporter*.

agents, the animal or vegetable fibers. They may be divided into natural [2] and synthetic dyestuffs, with the latter class now the most important; but the color chemist divides all dyestuffs rather on the basis of whether they can be applied to the fiber directly or whether preliminary treatment is necessary. From his point of view, dyestuffs may be divided into, a, direct dyes for cotton, b, direct dyes for wool and silk, and c, indirect dyes (developed dyes). This system of classification will be used in the following discussion, but first the meaning of the terms acid dyes and basic dyes will be made clear, because these expressions are in constant use.

Acid dyes are dyes which have a pronounced acid character; they are mainly sulfonic salts of azo bodies, or sulfonic derivatives of basic dyes; but acid dyes do not include the direct dyes for cotton, such as the benzidine class, even when these contain an acid group.

SO_3H
Metanil Yellow, an acid dye [3]
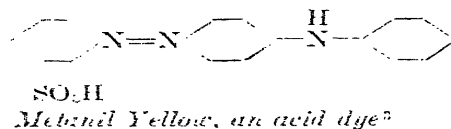
Basic dyes are hydrochlorides, sulfates or oxalates of organic bases; by the latter is meant a substance containing besides a benzene or other aromatic nucleus, an amino group or certain other groups containing nitrogen. Thus Bismarck Brown is the hydrochloride of a basic azo dye containing four amino groups:

Bismarck Brown, a basic dye
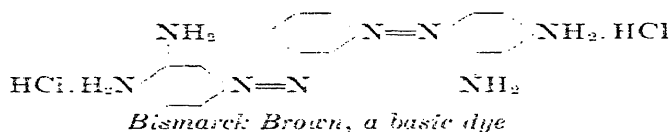
Other basic dyes are Malachite Green, which is a triphenylmethane dye, and Methylene Blue, a thiazine.

Direct Dyes for Cotton. Direct dyes for cotton are sodium salts of the benzidines, primulines, and a few others which contain the sulfonic (SO_3H) or carboxyl (COOH) group; such sodium salts have direct affinity for cotton, but the corresponding free acid dye has not. They are applied in a neutral or slightly alkaline solution. Examples: Congo Red and Brilliant Yellow.

Direct Dyes for Wool and Silk. Acid dyes are direct dyes for wool and silk; they are manufactured and shipped to the textile mill in the form of the sodium salts of such dyes, but the dye bath is made acid by adding sulfuric or acetic acid, so that the free dye is formed, that is, so that the sulfonic or carboxyl groups are free; in that state the dye is readily adsorbed by the animal fiber.

[2] Areas of cultivation and production figures for natural dyestuffs will be found on p. 54 of Putnam's *Economic Atlas*, London, George Philip and Son, Ltd., and New York, G. P. Putnam's Sons, 1925.

[3] The hexagon stands for benzene, C_6H_6; when a group (thus — SO_3H) is attached to the ring, it is understood that the hydrogen at that place is missing.

The basic dyes are direct dyes for wool and silk.

Indirect Dyes. The basic dyes are indirect dyes for cotton, for the latter must first be treated with tannin; the tannin is the mordant, and this use of basic dyes entitles them to a place among the mordant dyes. Among these latter, the tannin dyes are relatively unimportant.

Mordant Dyes. These comprise in addition to the above, those dyes which require preliminary treatment of the cotton with a metallic salt solution, followed by immersion in an ammonia solution, before the dye is applied. The ammonia treatment precipitates insoluble metallic hydroxides on the fiber and in the fiber; to this hydroxide, the dye becomes fixed in its turn. These insoluble, stable, colored compounds of metal and dye are termed "lakes." Alizarine, originally a natural dyestuff, now made altogether synthetically, is an example; it gives different colors with different salts, red with aluminum or tin, red-brown with calcium, blue-black with iron, and brown with chromium salts. A total of over 200 dyes, derivatives of alizarine or closely allied to it, form the class called alizarine dyes; the original alizarine, which is also the simplest, is still widely used; its formula is given in the next chapter.

Chrome Dyes. A direct dye is first applied to wool, the only fiber which is chrome dyed, in an acid bath; the wool is then given a treatment with a solution of sodium dichromate, resulting in the formation of a chrome lake on the fiber. Example: Diamond black.

Sulfur Dyes. Sulfur dyes are cotton dyes; they must be reduced with a solution of sodium sulfide (Na_2S), forming a soluble compound called leuco [4] compound which is adsorbed by the cotton. The dye is then re-oxidized, called development, in the air, and the insoluble sulfur dye is thus re-formed on the fiber itself. Such a process of re-forming the insoluble dye from its soluble leuco compound makes it extremely fast. Examples: Sulfur Black, Sulfur Blue.

Vat Dyes. Vat dyes are also, like the preceding sulfur dyes, cotton dyes; and like these, are insoluble in water. They are reduced with sodium hyposulfite [5] ($Na_2S_2O_4$) with formation of the soluble, colorless or slightly yellow leuco compounds, which are readily adsorbed by cotton. By exposing the treated cotton to the air, the original insoluble dyestuff reappears, fixed to the fiber so that it cannot be washed out. Examples are Indigo and Indanthrene; both are fast, Indanthrene extremely so. The formula of each of these substances is given in Chapter 28.

Developed Dyes. The developed dyes are insoluble. They are manufactured in stages, directly on the fiber. In the case of Para Red for example, the cotton fiber is treated with β-naphthol dissolved in caustic, and then passed through a diazotized paranitraniline solution; the formation of Para Red takes place on the fiber.

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[4] The term leuco compound is applied solely to the soluble reduced body formed from the insoluble dye by reduction.

[5] The correct chemical name is sodium hyposulfite. It is erroneously called sodium hydrosulfite or hydrosulfite in the trade.

OH

$$O_2N \underset{}{\bigcirc} N{=}N \bigcirc$$

Para Red
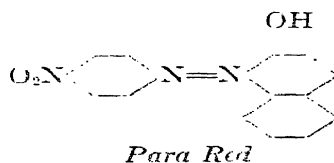
Another group of developed dyes involve direct dyeing by means of a direct dye, followed by diazotization on the fiber, and this in turn by coupling, so that another intermediate enters the molecule; it is a combination of direct dyeing and developed dyeing. These operations render the dye faster, that is, more resistant to washing and light. As example, Zambesi Black D involves the following operations: The direct dye whose molecule has the composition

$$H_2N \bigcirc \quad N{=}N \bigcirc \underset{OCH_3}{\overset{CH_2}{\bigcirc}} N{=}N \underset{HO_3S}{\overset{OH}{\bigcirc}} NH$$
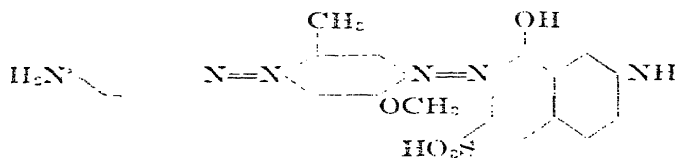
is applied to cotton as a direct dye; the color is black with a red tinge. The goods are now passed into a bath containing sodium nitrite and acid, when the amino group marked * is diazotized. Next the goods are passed through a solution of β-naphthol, which couples on the new diazo group, forming a full, deep black. The reaction for diazotization and the one for coupling are given in the chapter on dyes.

Concentration of Dye on the Fiber. A light shade is obtained with 1 per cent dyestuff on the fiber, heavier shades by using 2, 3, 5, or even 8 per cent. In all cases the dye bath is worked until exhausted, frequently with the addition of Glauber salt which tends to render the dye less soluble. It must be especially noted that by 1 per cent is meant 1 per cent of the weight of the fiber; the percentage has nothing to do with the strength of the solution.

Mixing to Type. Dyes are manufactured in batches of 1000 pounds, in most factories. No two batches are exactly alike. In order to obtain regularity of shade, a number of batches are mixed to give an average shade, which is called the type. Blending the various batches together is known as "mixing to type." A difference between the various batches would hardly be detected by the average person; to the trained eye it is evident.

PROCESS OF DIRECT DYEING WITH ACID DYES

Silk. Silk is placed in a bath containing the acid dye dissolved in the form of its sodium salt together with soap; enough dilute sulfuric or acetic acid is added to make the bath weakly acid. The dye bath is cold or lukewarm.

The dyes which may be used are, among many others: Ponceau, Crocein Scarlet, Eosine, Acid Fuchsine, Rhodamine, Rose-induline, Crocein Orange, Azoflavine, Methyl Yellow, Tartrazine, Patent Green, Alkali Blue, Patent Blue, Induline, Resorcin Brown, Naphthol Blue Black, Naphthol Black.

Wool. The dye bath is charged with the necessary amount of acid dye which dissolves, again in the form of a solution of the sodium salt; 2 to 4 per cent sulfuric or acetic acid is added in sufficient amount to liberate the free dye. The temperature is raised to $40°$-$50°$ C. and the wool introduced. Ten to 30 per cent Glauber salt $(Na_2SO_4 . 10H_2O)$, based on the weight of the wool, is added and the bath slowly heated to boiling by direct steam. The dye leaves the bath and attaches itself to the fiber. If the dyestuff goes on too fast, the cloth is blotchy; this may be prevented by adding aluminum sulfate or acid sodium sulfate instead of sulfuric acid.

A slight modification of the method consists in dissolving the sodium salt of the dye for the bath, introducing the wool, and then adding the acid very slowly, in small portions.

The dyes which among others may be used for wool are the same as listed under direct dyeing of silk with acid dyes.

Cotton. Before dyeing, cotton should be placed in a soap solution for an hour; it may then be introduced into the dye bath containing 2 to 5 pounds of dye for each 100 pounds of cotton, either as yarn in skeins, or as cloth; this is expressed as 2 to 5 per cent. One of the following salts is added to the dye bath: Glauber salt, common salt, borax, sodium phosphate, ammonium carbonate. The bath is then brought to a boil and maintained there for some time, until the bath is exhausted of dye. The function of the salt added is to diminish the solubility of the dye, and thereby hasten the exhaustion of the bath. The cotton is next washed and dried.

The dyes that are suitable are the members of the stilbene, benzidine, and primuline groups, such as Sun Yellow, Brilliant Yellow, Primuline Red, Congo Red, Direct Sky Blue, Direct Green B, Bordeaux, Scarlet and many others. Every shade is represented in these direct cotton dyes.

Many dyestuffs are precipitated by calcium and magnesium salts, so that a bath made up with ordinary ground water would result in precipitation of the dye; this is the reason why soft water must be used in the dye house.

MORDANTING WITH TANNIN

Mordanting with tannin concerns cotton chiefly. The cotton is placed in a hot water solution of tannin, and then in a lukewarm solution of tartar emetic, for instance. Antimony tannate is now fastened to the fiber, and is insoluble. The goods are next passed slowly through a solution of a basic dye.

The basic dyes listed in the following division are suitable for cotton mordanted with tannin.

If the cotton is treated with sulfonated castor oil before mordanting, the dyeing is more even, and the fiber is more pliant (softer). This is true of every cotton dyeing. The concentration of the oil is 10 grams per liter.

PROCESS OF DIRECT DYEING WITH BASIC DYES ON WOOL AND SILK

For wool and silk, no tannin is needed, for they already contain in the molecule an acid group. The basic dye is dissolved in water, the temperature raised to 50° C., and the wool or silk is introduced. The temperature is raised further gradually, over a period of half an hour to the boiling point, when the process is completed. The material is washed with water and dried.

Examples of basic dyes are: Fuchsine, Rhodamine, Safronine, Auramine, Phosphine, Malachite Green, Methylene Blue, Rosaniline, Mauve, Crystal Violet, Bismarck Brown.

The first synthetic dye was a basic dye, Mauve.

METALLIC MORDANTS

The procedure differs somewhat for the several fibers; the application to cotton is the most important. Cotton is treated with a solution of the metallic salt, such as aluminum sulfate. Next it is passed into
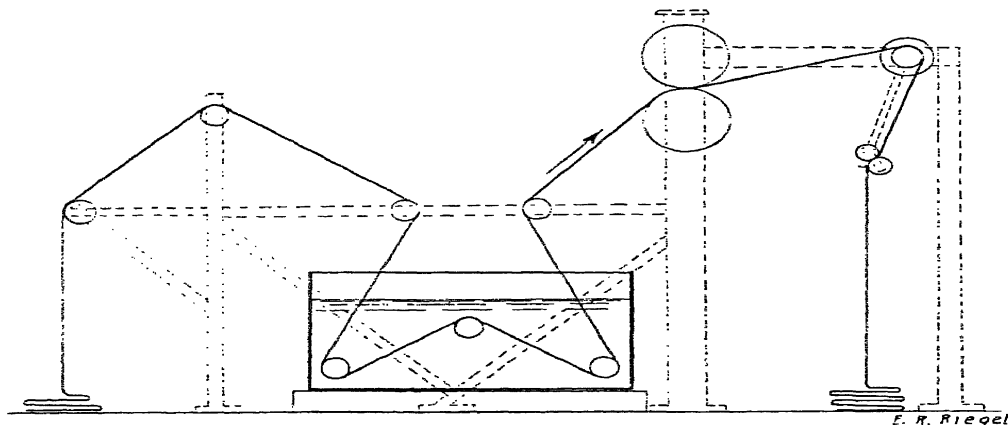
FIGURE 163.—The jigger.

an ammoniacal bath, and after that, into a solution of alizarine in ammonia water; sometimes the two latter baths are combined. Wool and silk can dissociate certain metallic salts, so that when they are placed in the salt solution, and boiled, the basic part of the dissociated salt deposits on the wool or silk. The rate of deposition is controlled by adding more or less potassium acid tartrate, which retards it. After that, the wool or silk is placed in the alizarine bath.

Examples of dyes applied with metallic mordants: Synthetic dyes—Alizarine, Alizarine Maroon, Purpurin, Anthrapurpurin, Anthracene Blue. Natural dyestuffs—Logwood, for blue and black, Cochineal, for red, Quercitron, for yellow.

In order to form lakes, hence be adaptable to this kind of dyeing, the molecule of the dye must contain two hydroxyl groups in the ortho position to each other, or one hydroxyl group with one of the following groups in the ortho position: carboxyl, COOH, nitroso, NO, azo, $N = N$, and imide, NH.

The process for vat dyes, developed dyes, sulfur dyes is similar to the processes described above; the special principles involved have been presented under the headings following Indirect Dyes.

APPARATUS

Wooden tubs are used for acid baths; for neutral and alkaline baths, wooden tubs are sometimes used, but iron and steel are more common. The dyeing may be done on skeins, or on the finished piece goods; in the latter case, a device known as the jigger is used, shown in Fig. 163.

DESIGN FORMATION

Patterns in color may be produced on the piece goods by printing with copper rolls, using one of the three principles stated below.

1. In direct printing, the thickened dye solution is applied directly onto the desired spot on the white piece goods; the remainder of the surface remains as before. For instance, a polka dot design may be printed in blue, from a copper roll having circular depressions filled with the dye solution. The blue dot on the white ground is formed directly. So that the color may not run at the edge of the dot, the solution is thickened by means of gelatin, starch, or other material.

Example on cotton: A basic dye mixed with tannin, acetic acid, and a thickener, is printed on directly; then the piece goods are steamed by passing them stretched over steam-heated hollow steel cylinders, washed, and dried.

2. In reserve printing, certain uncolored substances are printed onto the cloth at the spots which should remain white. The whole is then dyed, and in the dye bath these substances repel the dye.

3. In the discharge method, the cloth is first dyed all over, and then there is printed onto it a substance which can destroy the dye by oxidation or reduction, leaving the spots reached by it uncolored. After the printing, the cloth is steamed, washed, and dried.

As discharge materials, stannous chloride, zinc dust and caustic, sodium bisulfite, sodium hyposulfite ($Na_2S_2O_4$), and others may be used, thickened properly by an inert material so that the applied discharge material will not run. Basic dyes are discharged by applying a paste of

glucose, caustic, and a thickener; during the steaming, the reduction takes place.

Design formation by any one of these three methods is applicable to all fibers, with suitable modifications.

In Method 1 a mordant dye may be applied as well as a direct dye, working as follows: The dye and the mordant mixed cold do not react appreciably; the two mixed with a thickener are applied. In the subsequent steaming, the dye and mordant react, and fasten the produced lake onto the fiber.

In general, the printing is done with copper rolls etched in the design needed. In the depressions, the printing paste is fed constantly from a trough, while the surface of the roll is wiped clean by means of a scraper. It is a form of intaglio printing. The printing may be very elaborate: as many as 15 rolls have been applied to the same piece of cotton or silk. The consumption of the several fibers in 1936 follows (in millions of pounds): Cotton, 3468; wool, 384.5; silk, 57.9; artificial silk, 323.

Wetting-out Agents. In order to dye evenly, it is essential that the dye solution should reach every spot of the fiber at the same time; this will be the case only when the fibers are wetted at the same instant. The addition of certain substances favors this wetting, with subsequent even dyeing, and the materials have assumed an important rôle. The most important wetting-out agents are: soap, sulfonated castor oil, already mentioned, sulfonated naphthols, sulfonated abietene, Gardinol, Wet-It, Novo Naccosol.

PATENTS

U. S. Patent 1.865.701, manufacture of dyed rayon thread by precipitating the cellulose in filament form from a viscose solution impregnated with dyestuff in a reduced state and oxidizing the dyestuff to fix the color; 1,876,560, process of dyeing viscose rayon using tri-azo dyes. $(R_1 . N : N . R_1 . N : N . R_2 . N : N . R_3)$; 2,023,387; 1,998,550; 2,015,500; 1,992,160; 2,000,559, wetting agent.

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The intermediates are the link between the low-valued products of the distillation of coal tar and the valuable dyes. The manufacture of dye intermediates is the most brilliant success of synthetic organic chemistry.

Chapter 27

The Manufacture of Dye Intermediates*

The group of synthetic compounds called intermediates is the starting point for the manufacture of dyes; they form the raw materials for the dye industry; to put it still another way, the intermediates are the foundations of the dye constructions. The name is certainly appropriate, for they are the intermediate compounds between benzene,[1] naphthalene, and anthracene, on the one hand, and the brilliant and varied dyes, on the other.

That benzene, naphthalene, and anthracene are obtained by distilling coal tar,[2] the evil-smelling black liquid found in the hydraulic main of the illuminating gas plant, and similar plants, has been stated in Chapter 14; to name the intermediates, "coal-tar intermediates," and the dyes made from them, "coal-tar dyes," as is often done, is therefore quite correct. In themselves, benzene, naphthalene, and anthracene are of little value; but by the introduction of SO_3H, NO_2, NH_2, OH, alkyl or other groups into the molecule, replacing a hydrogen atom, the body becomes important and valuable; it is then an intermediate. The number of known intermediates is enormous; the number of the possible ones, greater still.

The transformation of benzene, naphthalene, and anthracene into these substituted bodies is done by a variety of operations, the most important of which may be divided into the following classes:

1. Nitration, the substitution of one or more hydrogens by NO_2.
2. Reduction, for instance, of NO_2 to NH_2.
3. Sulfonation, the substitution of one or more hydrogens by the sulfonic group, SO_3H.
4. Halogenation, the substitution of one or more hydrogens by Cl, Br, or I.
5. Alkylation, the substitution of hydrogen by an alkyl group, such as methyl, CH_3, or ethyl, C_2H_5.
6. Alkaline fusion, the substitution of the sulfonic acid group, SO_3H, by the hydroxyl group, OH.

In the discussion of these operations it is important to distinguish between various isomers produced, that is, bodies alike in the groups they contain, but differing in the relative position of these groups, as for example the two nitrotoluenes shown below under "nitration." Such a

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[1] Benzene is the same substance as benzol.

[2] The greater part of the benzene is obtained by "scrubbing" the gas from the distillation of coal, with oil, and recovering it from the oil by distillation.

distinction may seem a rather "nice" one, belonging to the scientific aspect of the subject, but it is in reality of the greatest practical importance, because the colors made later on by means of the separated isomers will differ; and to obtain pure colors, an intermediate free from its isomers must be used. It naturally follows that a firm producing impure intermediates, impure in the sense that a given body is still accompanied by its isomers, is likely to see its business dwindle.

It might be said further that two isomers often differ in a pronounced way in their properties, although the structural difference is so slight, for instance ortho-nitrotoluene is a liquid, while para-nitroluene is a white solid. The difference in properties is indeed sometimes slight, but there is always some difference in at least one property.

The compounds of carbon are exceedingly delicate; they react readily and always in several directions, for instance while nitrating, some oxidation is almost unavoidable. This circumstance, added to the difficulty with isomer formation, renders the choice of processes and their supervision so difficult that only men well-trained in scientific organic chemistry can choose and supervise successfully. In no other branch of industrial chemistry does plant practice follow so closely the purely scientific treatment of the subject. Only the products of industrial importance and the well-established plant processes are considered in this chapter.

The apparatus is comparatively simple; wooden, cast-iron, and steel vessels are used. High temperatures are rare, which might be inferred from the fact that carbon compounds burn, and before burning are destroyed by charring; the temperature of melting ice is used almost as often as that of steam.

The system of notation in this chapter is the customary one: the hexagon means benzene, C_6H_6, unless otherwise indicated; the double hexagon means naphthalene, $C_{10}H_8$. When a substituting group is written in, the hydrogen atom is understood to have been removed to make room for the entering group.

NITRATION

Ordinarily, nitration is performed in the cold, in order to render harmless the oxidizing tendency of the nitric acid. In many cases, the substance to be nitrated would be destroyed by nitric acid of full strength; to prevent this, it is diluted by means of concentrated sulfuric acid. This mixture is called "mixed acid",[3] and usually contains 25 to 30 per cent nitric acid; the rest is sulfuric acid with a small percentage of water. For example, the reaction for benzene is

$$C_6H_6 + HONO_2 = C_6H_5NO_2 + H_2O.$$
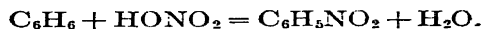
Nitrobenzene, an oil, is formed, and water. The sulfuric acid does not enter into reaction, but serves as a diluent and an absorbent for the

[3] Chapter 2.

water formed during the reaction, thus maintaining the strength of the nitric acid.

Not only are hydrocarbons such as benzene nitrated, but also, and very frequently, substances in which there already are present other substituting groups. If the group NH_2 is present, it must be "covered" during the nitration, even though the temperature is low, to prevent its oxidation and consequent loss. This "covering" is done by acetylation, and the acetyl group is removed after the nitration.

The groups already substituted in the molecule influence the position which the entering group takes, according to the following rule, given in two parts, with examples:

a. If any one of the groups CH_3, CH_2Cl, Br, I, OH, NH_2, and certain others is present, the nitro group enters mainly in the ortho and para position, sometimes only in the para position.

Examples:

| toluene (liquid) | ortho-nitrotoluene (liquid) | para-nitrotoluene (white solid) |

| phenol (solid) | ortho-nitrophenol (yellow solid) | para-nitrophenol (white solid) |
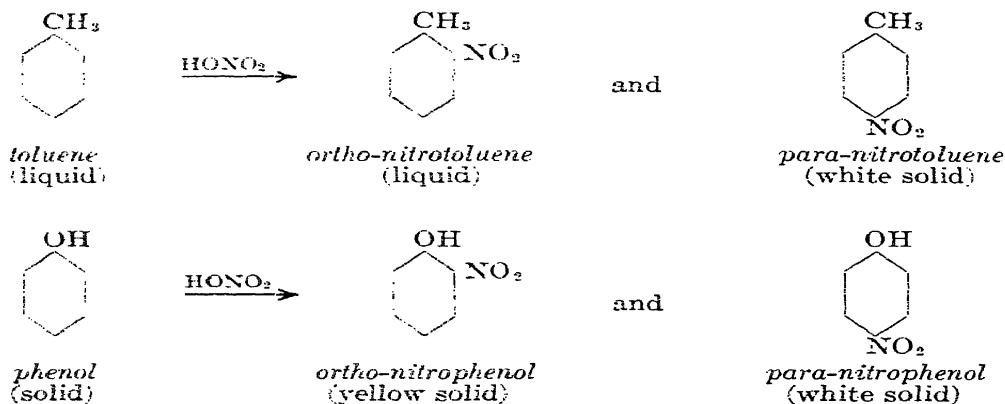
Ortho-nitrophenol and para-nitrophenol are isomers; they are separated by steam distillation, for the ortho body is volatile in the steam, while the para body is not, and therefore remains behind in the distilling vessel.

| chlorobenzene (liquid) | ortho-nitrochlorobenzene (low-melting solid) | para-nitrochlorobenzene (solid) |
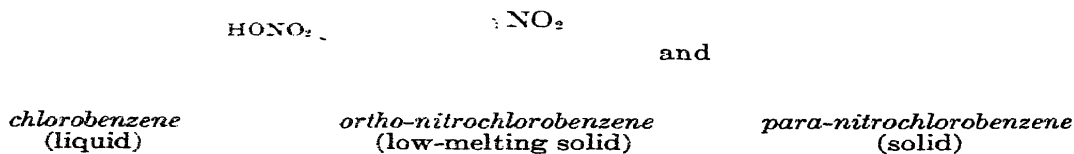
b. If there is present in the molecule any one of the following groups: NO_2, COOH, CHO (the aldehyde group), or SO_3H, the nitro group enters mainly meta. Example:

NO_2

nitrobenzene
(liquid)

$\xrightarrow{HONO_2}$

NO_2

NO_2

dinitrobenzene
(solid)

When nitrating benzene to nitrobenzene, an excess of nitric acid must be avoided, otherwise there is formed dinitrobenzene. The procedure is to run the mixed acid into the benzene, not the converse; this is a general rule, if a single substituting group is desired. About 2500 pounds of benzene are nitrated in one batch, and the time is 3 to 4 hours. Heat is evolved during the reaction and is removed as fast as generated by means of cooling pipes laid in the benzene, or by means of cold water (or brine) circulated in the jacket surrounding the vessel; towards the end of the reaction, warm water is circulated in the jacket. (See Fig. 164.)   Cast-

FIGURE 164.—Jacketed cast-iron nitrator, showing two impellers for agitation, and five cooling cells. (Courtesy of the Buffalo Foundry and Machine Co., Buffalo, N. Y.)
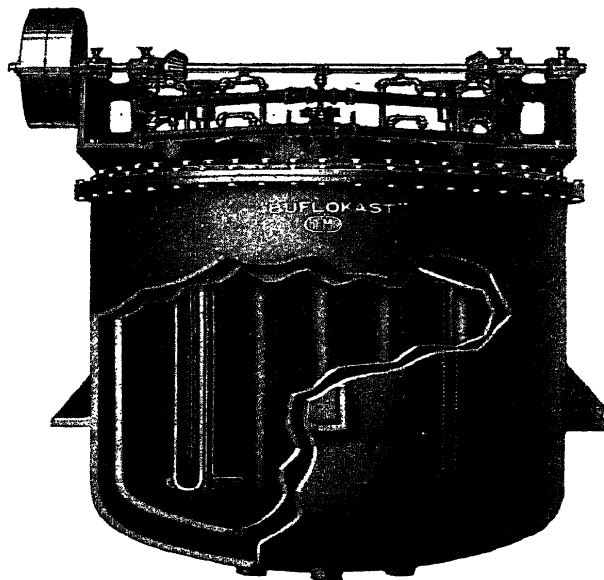
iron is used, since mixed acid does not attack it.   A stirrer is provided, for otherwise the benzene and the acid remain two separate layers.   After the action is complete, the nitrobenzene separates out as an oil over the acid, and is removed by decantation.   It is agitated with water or dilute alkali to remove small amounts of acid, and may then be distilled if pure nitrobenzene is desired.

When nitrated with enough acid to form two nitro groups, toluene gives two different dinitrotoluenes; the temperature is maintained at 35° C.:

toluene
(liquid)
→ 2HONO₂ →
(yellow solid)
and
(yellow solid)
trace
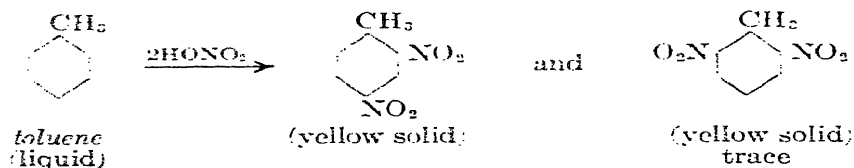
Naphthalene treated with the proper amount of mixed acid to form one nitro group gives only α-nitro-, never β-nitronaphthalene

naphthalene
(white solid when pure)
→ HONO₂ →
α-nitronaphthalene
or 1-nitronaphthalene
(yellow solid)
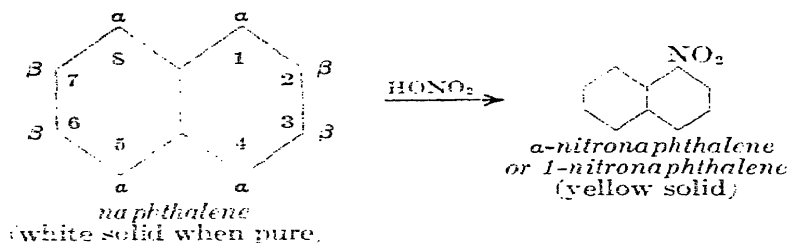
On further nitration, the mono-nitro body gives 1,5 or 1,8 dinitronaphthalene; the temperature is 70° C.; all three bodies are solids.

1-nitronaphthalene
→ HONO₂ →
1,5 dinitronaphthalene
and
1,8 dinitronaphthalene
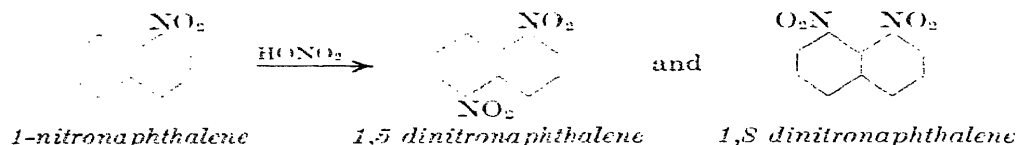
Anthraquinone nitrated for one nitro group gives only α-nitroanthraquinone at 50° C.; a second group enters again α, producing the isomers 1,5 and 1,8 dinitroanthraquinone at 80° C.; all are yellow solids.

anthraquinone
→ HONO₂ →
1-nitroanthraquinone
→ HONO₂ →
dinitroanthraquinone
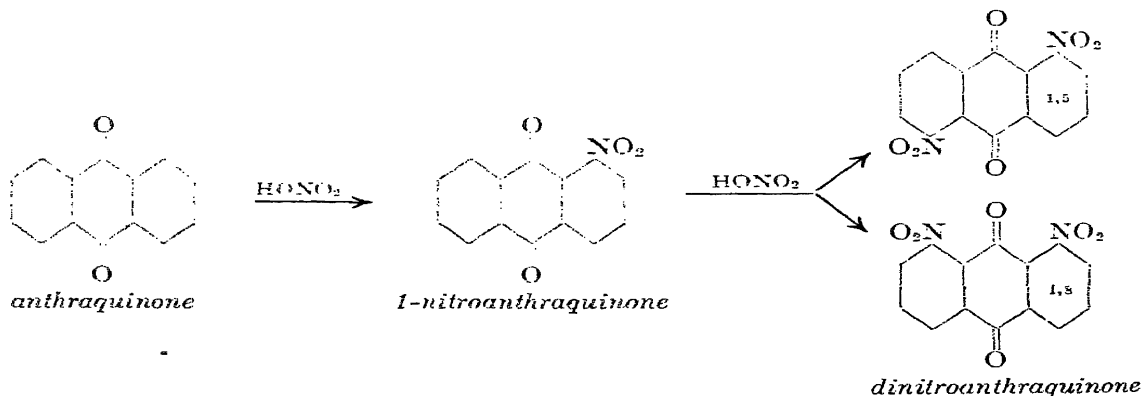
Hence, according to the amount of acid used, there may be produced mono-, di-, or even trinitroanthraquinone compounds.

These nitrations are performed in cast-iron or steel vessels with steel agitators: a liquid requires no pre-treatment; a solid is dissolved in concentrated sulfuric acid, and this solution then treated with the mixed acid.

REDUCTION

Among reductions, that of the nitro group, NO_2, to the amino group, NH_2, is a frequent and important one; several reducing agents may be used:

a. Iron turnings or powder and hydrochloric acid are generally used: less frequently tin or zinc with hydrochloric acid. The theoretical reaction is

$$\langle\!\!\!\!\!\rangle NO_2 + 3Fe + 6HCl = \langle\!\!\!\!\!\rangle NH_2 + 3FeCl_2 + 2H_2O$$

nitrobenzene   *aniline*
(liquid)   (liquid)
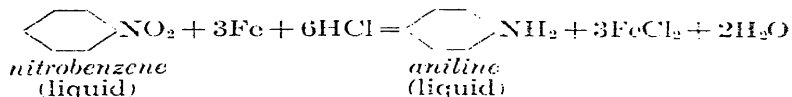
But in practice, one-fortieth of the amount of acid required by this reaction is sufficient, because the ferrous chloride formed catalyzes the reaction

$$2Fe + \langle\!\!\!\!\!\rangle NO_2 + 4H_2O = 2Fe(OH)_3 + \langle\!\!\!\!\!\rangle NH_2$$
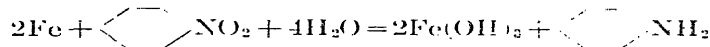
The nitrobenzene is placed in the reducer, a vertical cylindrical vessel provided with cover, steam jacket and a stirrer; the iron turnings [4] or powder and the hydrochloric acid are added gradually, in small portions. A brisk reaction, but not violent, is maintained by means of steam

FIGURE 165.—A vacuum shelf drier, with condenser and vacuum pump. The shelves are hollow and receive steam. Such driers are used for intermediates and dyes. (Buflovak.) (Courtesy of the Buffalo Foundry & Machine Co., Buffalo, N. Y.)
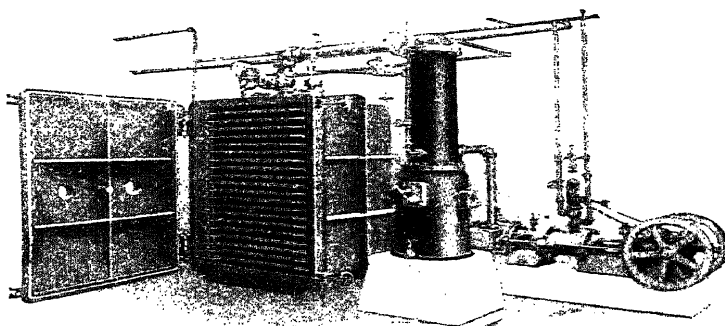
circulated in the jacket, or blown into the charge directly. A condenser returns to the reducer any vapors which pass out. After the nitrobenzene is completely changed to aniline, a strong current of live steam is sent into the charge; a mixture of steam and aniline vapors passes out to the condenser and is collected in storage tanks. The bulk of the aniline separates as a lower layer and is drawn off; the water over it still

[4] Cast-iron turnings, crushed in a hammer mill to pass through a 10-mesh screen, are to be preferred.

contains aniline, which must be recovered by distilling this "aniline water" again, or by extracting it with nitrobenzene. The iron hydroxide sludge is washed out of the reducer through a side outlet by means of flushing. A reducer 6 feet in diameter and 10 feet high takes a charge of 5000 pounds of nitrobenzene in one batch, and requires about 10 hours for the reduction. The aniline may be redistilled, when it is water white. There are many modifications of this method of reduction. The condenser consists of iron pipes laid in cold water.

Aniline is made from chlorbenzene, by treating the latter with ammonia in the presence of cuprous salts as catalysts. It is a continuous process, with ammonium chloride as a rather annoying by-product.[5]

Aniline hydrochloride is a widely used white solid, and is made by treating aniline with hydrochloric acid.

The reduction of nitrobenzene may be performed in acid, neutral, or alkaline solution and the products are in each case different. In acid solution, aniline is produced, as described above. In neutral solution, by means of zinc and ammonium chloride, there results phenylhydroxylamine:
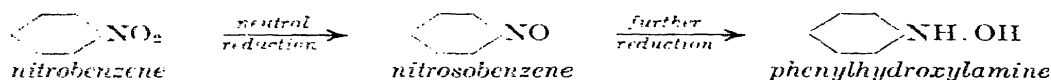
If allowed to go too long, the phenylhydroxylamine is further reduced to aniline.

In alkaline solution azobenzene is formed, itself the starting point for benzidine:
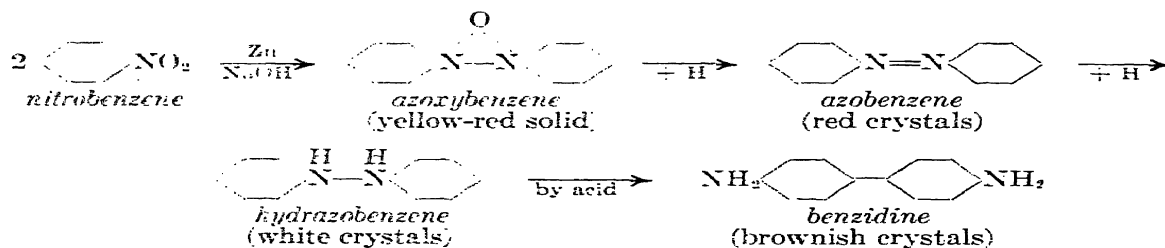
b. Alkaline reductions are performed for instance by means of zinc dust and caustic in water, or in hydrous alcohol; in addition to the example above, the following may be given:
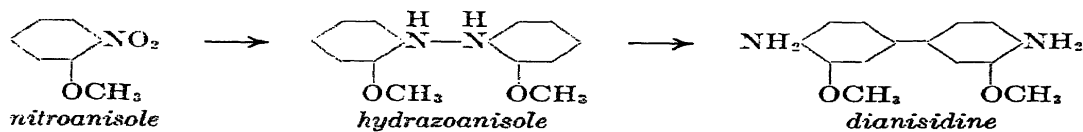
c. Sulfur dioxide as such, or its salt, bisulfite of sodium, may be used for reducing; for instance, quinone to hydroquinone. When nitro or

[5] U. S. Patents 1,726,170-3; reissue 17,280

nitroso bodies are treated, the reduction is frequently accompanied by the simultaneous introduction of the sulfonic group.

$$HO\langle\rangle NO \longrightarrow HO\langle\rangle \overset{SO_3H}{\underset{SO_3H}{NH_2}}$$

para-nitrosophenol

$$\overset{NO_2}{\langle\rangle}NO_2 \longrightarrow \overset{NO_2}{\underset{SO_3H}{\langle\rangle}}NH_2$$

meta-dinitrobenzene

$$\langle\langle\rangle\rangle\overset{NO}{OH} \longrightarrow \overset{NH_2}{\underset{SO_3H}{\langle\langle\rangle\rangle}}OH$$

nitrosonaphthol
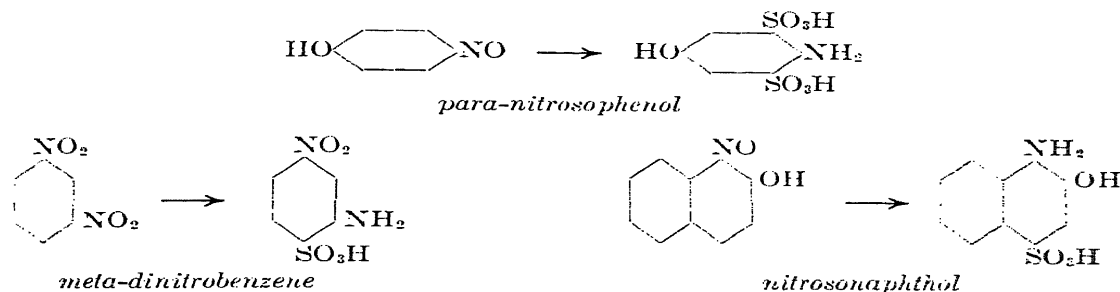
d. Sodium sulfide (Na$_2$S) is extremely valuable for reductions, also the disulfide, prepared by dissolving sulfur in a solution of sodium sulfide. For "partial reduction," that is, for the reduction of only one nitro group in a compound which has two, for instance dinitrobenzene, sodium sulfide is usually chosen. The sodium sulfide is dissolved in alcohol and placed

$$\overset{O_2N}{\langle\rangle}NO_2 + Na_2S + H_2O \longrightarrow \overset{O_2N}{\langle\rangle}NH_2 + Na_2SO_2$$

dinitrobenzene *meta-nitraniline*
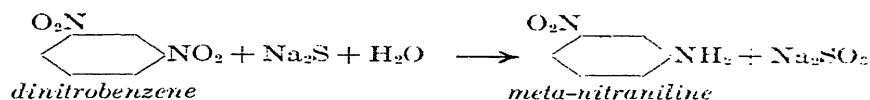
in a steam-jacketed reducer; the dinitrobenzene is added either solid, or also dissolved in alcohol. The mixture is maintained at boiling temperature for two hours; then the alcohol is distilled off, condensed and collected in a similar reducer and is ready for the next batch; the loss of alcohol is slight. There remains in the first reducer the meta-nitraniline mixed with the inorganic salt; the mass is agitated with water which dissolves the latter. The suspension is pumped into a filter press where the meta-nitraniline is obtained as a moist cake; it is dried on trays in a vacuum drier.

The isomer, para-nitraniline, is made by nitrating aniline after covering the amino group by acetylation; in other words, by nitrating the white solid, acetanilide [6]; the temperature is maintained between 6° and 8° C.

SULFONATION

Sulfonation is performed in order to render insoluble compounds soluble in water or alkalies; or it may be performed as the first step in the introduction of the hydroxyl group, which is completed by subsequent alkaline fusion.

By direct sulfonation is meant the treatment of the substance with fuming sulfuric acid; in the case of benzene, an oleum containing 8 per cent free SO$_3$ is added gradually, in order to offset the dilution caused by the water of reaction:

$$C_6H_6 + OHSO_2H = C_6H_5 . SO_3H + H_2O.$$
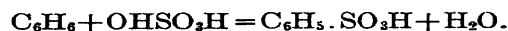
[6] Another method is given under halogenation.

The temperature is maintained at 30° C. until near the end, when it is raised to 50°; the vessel used is shown in Figure 166. After the action is over, the charge is drowned in water, and the benzene sulfonic acid salted out; or, if the product is to serve for making phenol by alkaline
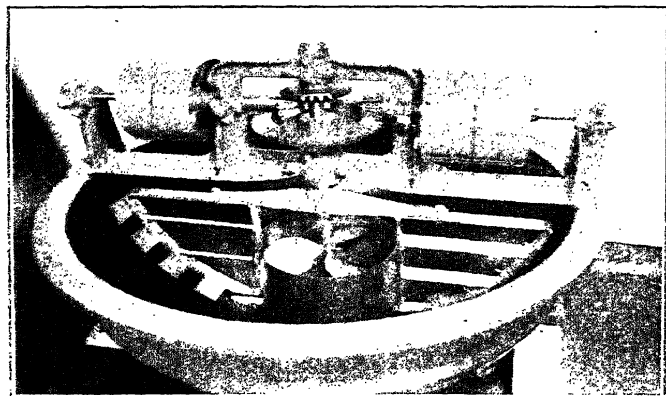
Figure 166.—A jacketed Dopp sulfonator, with scraper and propeller. Positive scraping of cooling of surface cuts in half the time required when using propeller only. Scraper on hollow shaft, low-speed; propeller on inner shaft, high speed. (Courtesy Sowers Manufacturing Co., Buffalo, N. Y.)

fusion, lime is added; the free sulfuric acid is precipitated as sulfate which is removed by filtration. The liquor contains the calcium salt of the sulfonic acid; it is treated with soda ash, forming the sodium salt and precipitating calcium carbonate. After another filtration, the sodium salt in solution may be isolated by evaporation.

If there is present in the molecule one of the three groups, NO_2, COOH, or SO_3H, the entering sulfonic group will take the meta position, in accordance with the rule for orientation given under nitration:
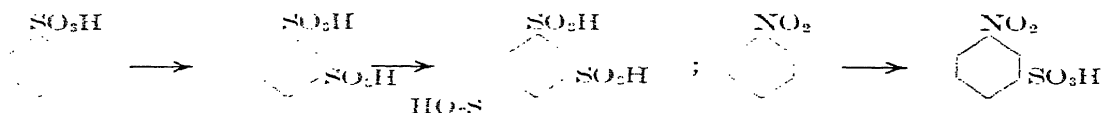
If the methyl group is present the result is different, but still in agreement with the rule; ortho and para derivatives are formed:
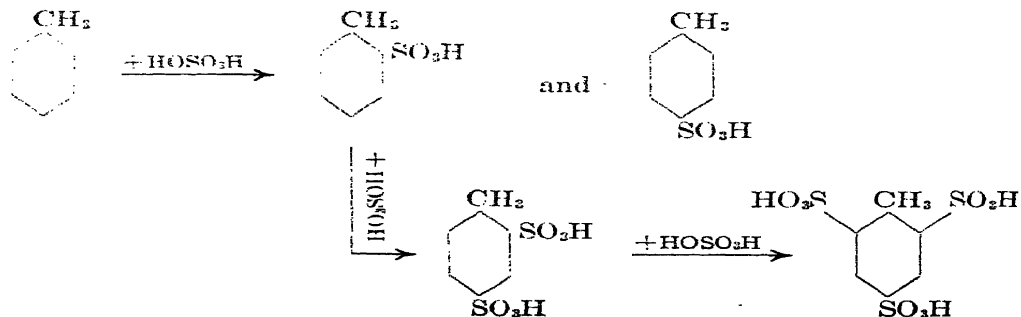
By sulfonating aniline, only para-sulfonic benzene, called sulfanilic acid, is formed; no covering of the amino group is necessary; but if the aniline group is methylized, the sulfonic group enters meta:

| aniline | sulfanilic acid (solid) | dimethylaniline (liquid) | dimethylaniline-meta-sulfonic acid |
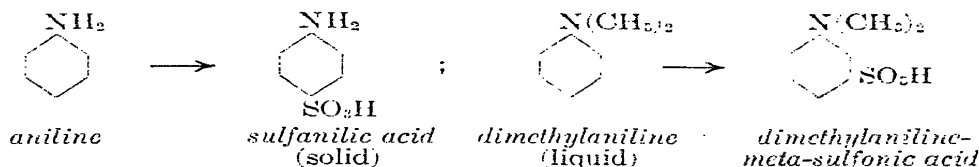
Indirect sulfonation may be done in various ways; for instance bodies with the quinonoid structure may be sulfonated by $NaHSO_3$, with simultaneous reduction of any nitroso or nitro group present to the amino group. Nitroso phenol is made by adding acid to sodium nitrite and phenol dissolved in caustic soda.

nitrosophenol   *disulfonic-para-aminophenol*
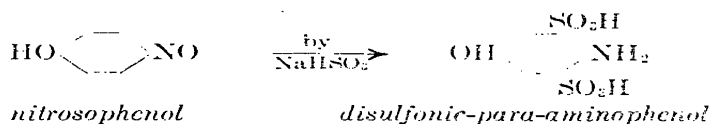
By reducing the same para-nitrosophenol with sodium sulfide (Na_2S), para-aminophenol is produced.

Direct sulfonation of naphthalene gives a mixture of α and β derivatives by varying the temperature; one or the other may be made to predominate; thus at 100° C. there is formed 95 per cent α and 5 per cent β; while at 170° C. 18 per cent α and 82 per cent β is formed.
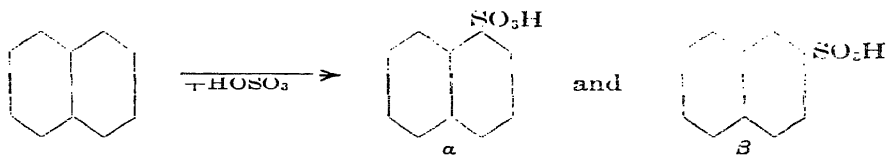
The naphthalene is melted and the acid run into it, in order to avoid the formation of disulfonic derivatives; the amount of acid is the calculated amount for one group. The water formed during the reaction retards it but does not prevent it; a definite amount of oleum (8 per cent SO_3) is added towards the end in order to hasten it.

Sulfanilic acid and naphthionic acid are prepared in an indirect way frequently, namely, by forming the corresponding sulfate salt and heating the latter in thin layers, when an intermolecular change takes place and the sulfonic group enters the nucleus, in both cases in the para position; this is the "baking process."

$NH_2 \cdot H_2SO_4$ $\xrightarrow[\text{170°–190° C}]{\text{heated to}}$ NH_2 ... SO_3H $+ H_2O;$ $NH_2 \cdot H_2SO_4$ $\xrightarrow{\text{heated}}$ NH_2 ... SO_3H $+ H_2O$

aniline sulfate   *sulfanilic acid*   *α-naphthyl-amine sulfate*   *naphthionic acid*
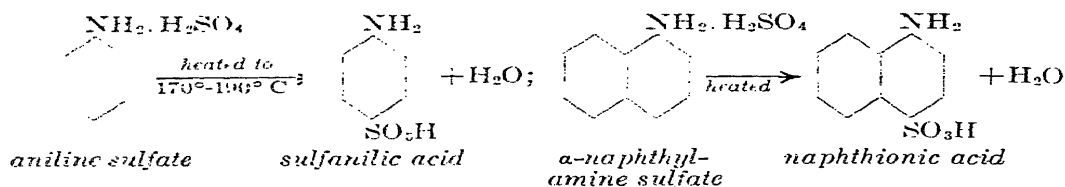
On direct sulfonation *α*-naphthyl amine gives mainly naphthionic acid; *β*-naphthyl amine forms a mixture of 2-5 and 2-8 sulfonic acids:

NH_2 $\longrightarrow$ NH_2 ... SO_3H and HO_3S ... NH_2
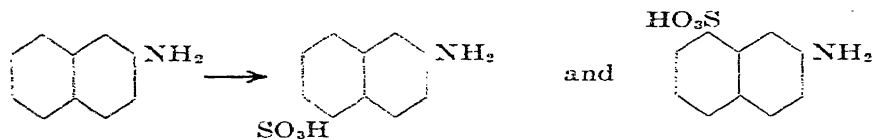
On sulfonating *β*-naphthol, two isomeric monosulfonic acids are formed:

HO_3S ... OH HO_3S ... OH

Schaeffer's acid (2-6)   *Crocein acid (2-8)*
(solid)   (solid)

By further sulfonation two isomeric disulfonic acids form:

HO_3S ... OH ... SO_3H HO_3S ... OH ... HO_3S

R acid (2-3-6)   *G acid (2-6-8)*
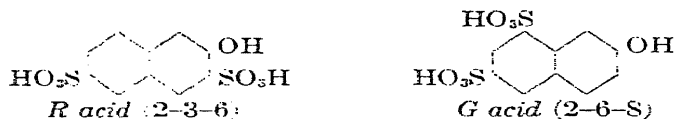
These two differ in that a diazo body couples with them at different rates; with the R acid. rapidly; with the G acid, slowly.[7] Schaeffer's acid and Crocein acid show the same difference.

Anthraquinone, a yellow solid, is sulfonated by suspending it in oleum containing 45 per cent free SO_3, hence very strong oleum, and heating to 150° C. for one hour; the resulting melt is run into water and neutralized with caustic soda while hot. On cooling, the sodium salt of the *β*-sulfonic-anthraquinone separates as a salt resembling metallic silver. For that reason it is called silver salt, important chiefly in the manufacture of alizarine.

O ... α β ... O $\longrightarrow$ O ... 8 7 6 5 1 2 3 4 ... SO_3H ... O *Silver salt*
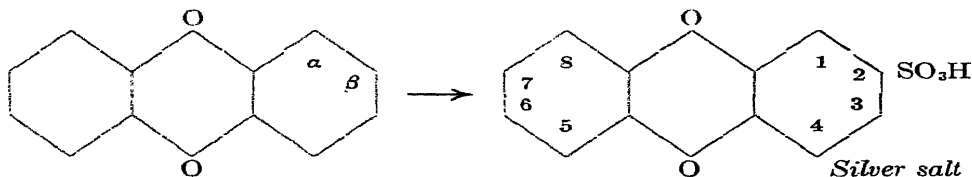
[7] R acid gives redder dyes, G acid dyes more on the yellow, hence the designations, from the German "rot" and "gelb."

Sulfonated further, a mixture of the 2,6 and 2,7 disulfonic anthraquinones are formed.

If the sulfonation is performed in the presence of mercurous sulfate, different products are obtained: a single sulfonic group enters at α or 1; two groups enter to form the 1,5 and 1,8 disulfonic anthraquinones.

HALOGENATION

Of the three halogens, chlorine is the most widely used, because of its comparative cheapness. As a rule, chlorinations are performed by dried chlorine gas, that is, by direct chlorination, with or without a catalyzing agent.

Chlorobenzene is made by passing a stream of dried chlorine into benzene in the presence of 1 per cent ferrous chloride; some para-dichlorobenzene is formed at the same time:

chlorobenzene
(liquid)

;

para–dichlorobenzene
(white solid)
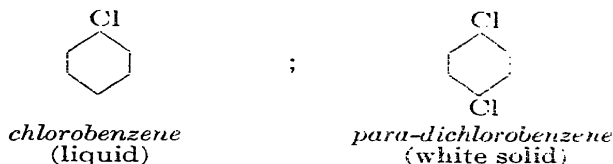
When passed into boiling toluene contained in a stoneware or enameled vessel, the chlorine enters the methyl group, producing a mixture of mono-, di-, and trichlorotoluene, all liquids; dichlorotoluene treated with water in the presence of calcium carbonate gives benzaldehyde; trichlorotoluene under the same treatment gives benzoic acid.

benzaldehyde
(liquid)

;

benzoic acid
(white solid)

In this chlorination an iron vessel cannot be used, for the iron would cause a portion of the chlorine to enter the nucleus.

The hydrogen chloride formed in the chlorination might cause side reactions; in order to prevent this, in many reaction mixtures calcium carbonate is suspended. The calcium chloride which forms does not interfere.

$$C_6H_6 + Cl_2 = C_6H_5Cl + HCl$$
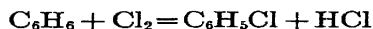
There are many catalytic agents in use such as SO_2Cl_2 (sulfuryl chloride), PCl_5 (phosphorus pentachloride), $SbCl_5$ (antimony pentachloride), I (iodine), Fe (iron); furthermore sunlight, ultra-violet rays, and temperature have an influence on the course of the reaction.

By means of the halogen, the reactivity of the compound is increased; the chlorine is more or less readily substituted by other groups. In the

benzene or naphthalene nucleus, the chlorine is the more readily substituted the greater the number of negative groups, such as nitro groups, present. Thus with ammonia, chlorobenzene does not react, but paranitrochlorobenzene does, forming para-nitraniline.

$$Cl \langle \rangle NO_2 + NH_3 \longrightarrow NH_2 \langle \rangle NO_2 + HCl.$$
(solid)   (solid)
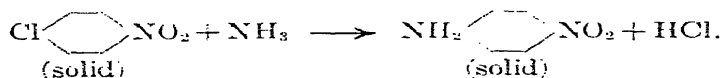
In acetic acid, one, two, or three of the hydrogen atoms in the methyl group may be replaced by direct chlorination of the warm liquid in the presence of sulfur:

$CH_2ClCOOH$	$CHCl_2COOH$	CCl_3COOH
mono-chloroacetic acid	*di-chloroacetic acid*	*tri-chloroacetic acid*
(solid)	(liquid)	(solid)
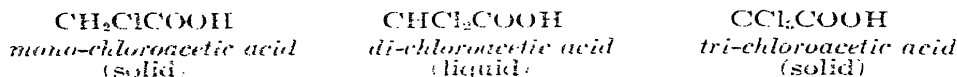
ALKYLATION

The alkyl groups, such as the methyl group, may be introduced into the amino group of an aromatic amine by heating it under pressure with methanol, in the presence of mineral acids.

$$C_6H_5 . NH_2 + CH_3OH \longrightarrow C_6H_5 . NH . CH_3 + H_2O$$
aniline   *mono-methylaniline*
                (liquid)
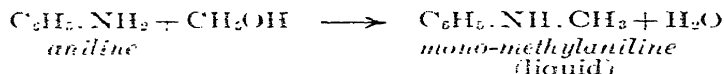
Another method used at present is the treatment with methyl sulfate or ethyl sulfate in the cold, in presence of caustic soda:

$$C_6H_5 . OH + (CH_3)_2SO_4 \longrightarrow C_6H_5 . OCH_3 + H . CH_3 . SO_4$$
phenol   *methyl*   *anisole*   *methyl*
      sulfate   *sulfuric acid*
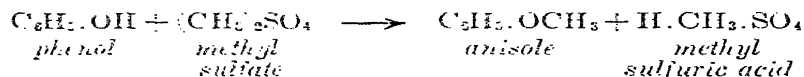
ALKALINE FUSION

By means of an alkaline fusion, a sulfonic group is replaced by a hydroxyl group; there are other methods to introduce the hydroxyl group, but this is the simplest. The sulfonic acids is dissolved in a concentrated solution of sodium hydroxide or caustic in a covered cast-iron pot provided with a scraping stirrer and heated externally by steam, oil bath, or an open fire. The water is evaporated, and on continued heating, the mass fuses; the temperature varies for the various reactions, but lies between 190° and 350° C.

Phenol is manufactured by fusing benzene sulfonic acid with caustic; this reaction as well as another are discussed in Chapter 35.

$$C_6H_5SO_2Na + 2NaOH = C_6H_5 . ONa + Na_2SO_3 + H_2O$$

The sodium phenolate formed is treated with acid to liberate the phenol. Resorcinol is made by alkaline fusion:

$$\underset{\substack{\text{Cl} \\ \\ \text{SO}_3\text{H}}}{\bigcirc} \xrightarrow[\text{fusion}]{\text{by NaOH}} \underset{\substack{\text{ONa} \\ \\ \text{ONa}}}{\bigcirc} \rightarrow \underset{\substack{\text{OH} \\ \\ \text{OH}}}{\bigcirc}$$

resorcinol
(white solid)
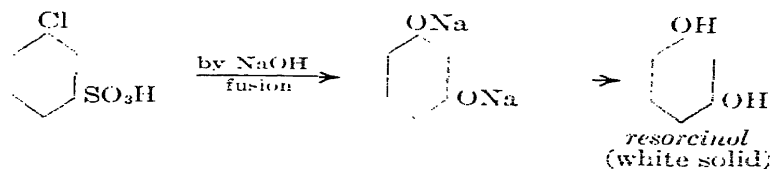
FIGURE 167.—Cast-iron fusion pot for alkaline fusions. with agitator.
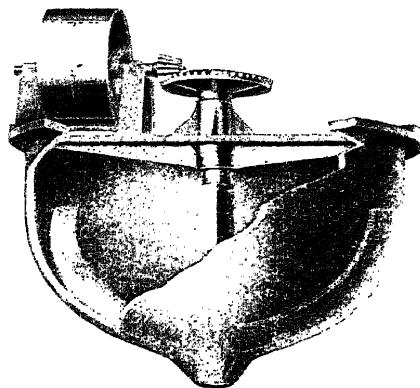
β-naphthol is made by fusing the corresponding sulfonic naphthalene with caustic; the naphtholate is treated with carbonic acid, and the precipitated β-naphthol is purified by distillation in vacuum.

$$\underset{\text{SO}_3\text{H}}{\bigcirc\bigcirc} \rightarrow \underset{\text{ONa}}{\bigcirc\bigcirc} + H_2CO_3 \rightarrow \underset{\text{OH}}{\bigcirc\bigcirc}$$
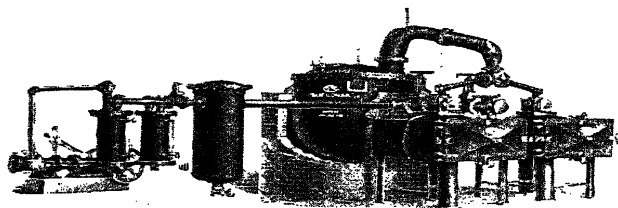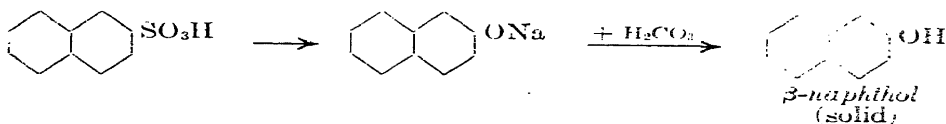
β-naphthol
(solid)

FIGURE 168.—A β-naphthol still. (Courtesy of Buffalo Foundry and Machine Company, Buffalo, N. Y.)

α-naphthol is not made from the sulfonic derivative, because there is always formed some of the β-naphthol at the same time; instead, α-naphthyl amine sulfate is heated with excess water in closed lead-lined vessels to 200° C. for two hours. On cooling the α-naphthol crystallizes out.

$$\underset{\text{NH}_2 \cdot \text{H}_2\text{SO}_4}{\bigcirc\bigcirc} + H_2O \rightarrow \underset{\text{OH}}{\bigcirc\bigcirc}$$
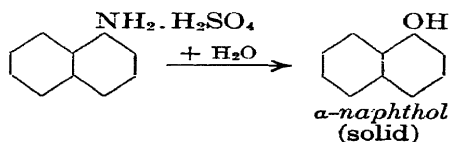
α-naphthol
(solid)

Sometimes the action of the concentrated fused caustic is too great; in that case a water solution is used and the reaction mix heated under pressure:

trisulfonic α-naphthol — 60% NaOH under pressure → chromotropic acid
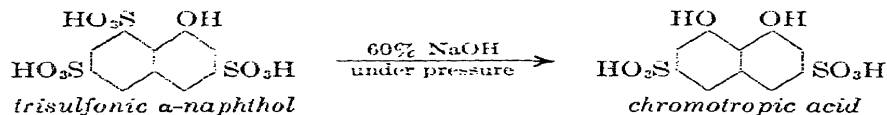
Sulfonated naphthyl amines may be fused with caustic to give aminonaphthols and aminonaphthol-sulfonic acids; the amino group is not destroyed. Examples:

1,amino-trisulfonic-naphthalene — by NaOH fusion → H acid

2,amino-5,7-disulfonic-naphthalene — by NaOH fusion → J acid
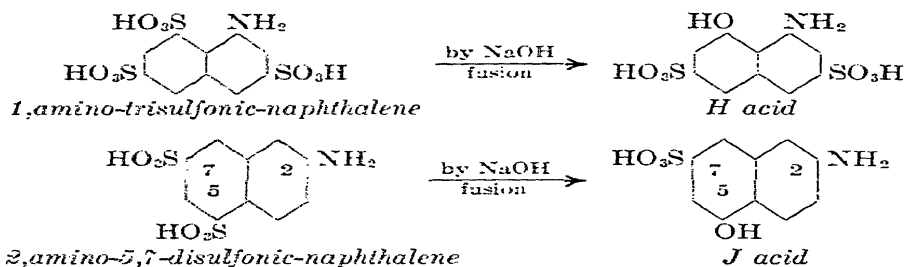
The aminonaphthol-sulfonic acids are almost indispensable for the manufacture of azo dyes; there is no azo dye of importance which does not contain at least one naphthalene derivative.

Anthraquinone β-sulfonic acid may be changed to the hydroxyl compound by heating with milk of lime:

anthraquinone sulfonic acid — Ca(OH)₂ and water → β-hydroxy-anthraquinone
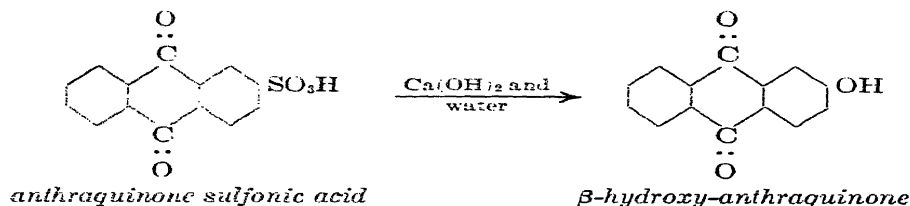
The same sulfonic acid fused with caustic gives the di-hydroxy derivative in addition to the mono-hydroxy compound. By adding an oxidizer such as potassium nitrate or chlorate, a high yield of the dihydroxy anthraquinone forms; this is alizarine, which is discussed further in the next chapter.

anthraquinone sulfonic acid — NaOH fusion → alizarine
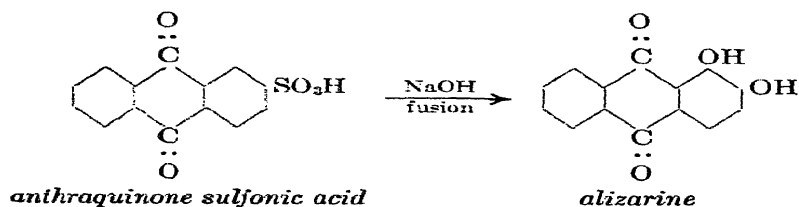
OTHER IMPORTANT INTERMEDIATES

Diphenyl amine is made by heating aniline and aniline hydrochloride in a closed cast-iron vessel, an autoclave, for 32 hours at 200° C.; the melt is extracted with weak hydrochloric acid, and distilled under reduced pressure. This body is important not only as an intermediate but also as a stabilizer for gun-cotton.

aniline (liquid) + *aniline hydrochloride* (white solid) ⟶ *diphenylamine* (when pure, white solid) + *ammonium chloride*
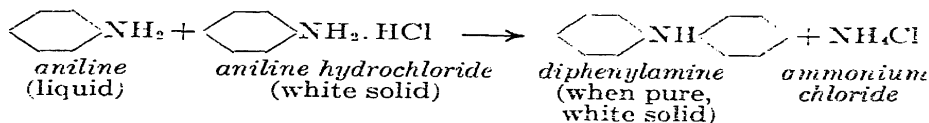
Salicylic acid is made by dissolving phenol in sodium hydroxide, evaporating to absolute dryness; passing in carbon dioxide under pressure, and maintaining the temperature near 150° C. in a cast-iron closed vessel. The charge is dissolved in water, and acidified to precipitate the free acid, which may be purified by distilling at low pressure.

sodium phenolate + CO_2 ⟶ *intermediate compound* ⟶ *sodium salicylate* ⟶ *salicylic acid* (white solid)
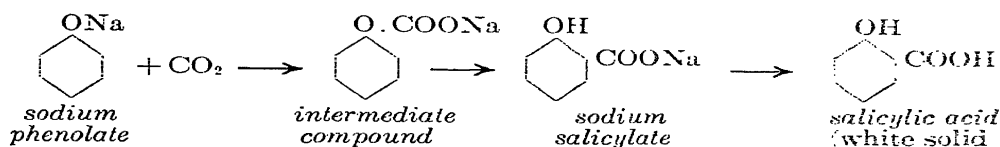
Anthraquinone is made by oxidizing anthracene with sodium dichromate and sulfuric acid. The crude anthracene, $C_{14}H_{10}$, is purified by pressing while warm; the press cake is atomized by steam, and the finely divided naphthalene suspended in boiling water is treated with dichromate and sulfuric acid, added in portions. The mixture is run, while still hot, into water in order to dilute the acid; the anthraquinone is filtered and washed. Two other methods for purification are given in Chapter 25.

By heating phthalic anhydride and benzene in presence of aluminum chloride, anthraquinone is formed.

phthalic anhydride   *benzene*   *anthraquinone* (pale yellow solid)
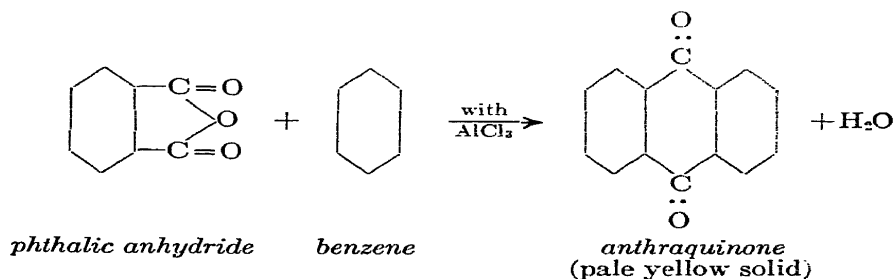
An intermediate compound containing the aluminum is first formed, and from this, by removal of basic aluminum chloride, anthraquinone. Production figures for some typical intermediates are given in Table 59.

TABLE 59.—*The United States Production for a Few Intermediates and Their Raw Materials for 1935.*

	Quantity	Cents per pound
α-Naphthol	0.9 million pounds	53
Diphenyl guanidine	1.2 million pounds	33
H acid	2.98 million pounds	..
Aniline oil	32.6 million pounds	11
Naphthalene	46.6 million pounds	4
Nitrobenzene	48.2 million pounds	8
		per gallon
Benzol, not including motor fuel.....	24.1 million gallons	13

* Census of Dyes, U. S. Tariff Commission.

OTHER PATENTS

U. S. Patent 1,841,622, azo dye intermediates and the dyes therefrom; 1,834,876, production of dyestuff intermediates, di-anthraquinonyl derivatives containing chlorine, bromine and sulfonic acid groups in the 2-2 position; 2,029,315, trifluoromethyl-phenyl-azo-diamino pyridines and process for making same.

PROBLEMS

1. 2500 pounds of benzene are nitrated in one batch, with a 90 per cent recovery, to nitrobenzene which is then reduced to aniline by Fe and HCl. The aniline recovery based on the nitrobenzene is 88 per cent. How much aniline is obtained? How much Fe and HCl will be required?

2. Diphenyl amine is made by the process given in the text. In order to produce 1200 pounds every day, how much of the two raw materials will be needed? The yield comes to 88 per cent. How much ammonium chloride will be left in the still?

From information obtained through the reading references, what size apparatus and what kind would you propose?

READING REFERENCES

"The manufacture of organic dyestuffs," André Wahl, translated from the French by F. W. Atack, London, G. Bell & Sons, Ltd., 1914.

"Aniline and its derivatives," P. H. Groggins, New York, D. Van Nostrand Co., 1924.

"Coal tar dyes and intermediates," E. D. B. Barnett in the series on Industrial Chemistry edited by Samuel Rideal, London, Baillière, Tindall & Co.

"Equipment for nitration and sulfonation," R. Norris Shreve, *Ind. Eng. Chem.*, 24, 1344 (1932).

"Intermediates for dyestuffs," A. Davidson, New York, D. Van Nostrand Co., 1926.

"The synthetic dyestuffs and the intermediate products from which they are derived," J. C. Cain and J. F. Thorpe, London, Chas. Griffin and Co., 1933.

Natural dyes have been almost entirely displaced by the synthetic organic dyes, which supply every shade imaginable, and which have a brilliancy never approached by natural dyes. The intermediates discussed in the previous chapter form the components of the artificial or synthetic dyes; how these component parts are assembled will be described in this chapter.

Chapter 28

The Manufacture of Dyes *

An organic dye is a colored carbon compound which has the property of dyeing permanently, with or without mordant, animal and vegetable fibers. Dyes are derivatives of carbon-containing radicals in which at least one ring structure, such as the benzene or naphthalene nucleus, is contained. Other chemical elements are present in the dye molecule, such as hydrogen, oxygen, nitrogen, and sulfur.

There are several classes of dyes, each of which contains one or more characteristic groups, a chromophore, such as $- N = N -$ for the azo class. The organic body containing the chromophore is a chromogen, such as azobenzene
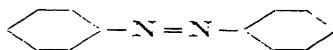
By introducing one or more of the following salt-forming groups (auxochromes), hydroxyl (OH), amino (NH$_2$), carboxyl (COOH), the chromogen becomes a dye.[1]

The shades and nuances of the dyes depend, on one hand, on the nature and number of the chromophore and salt-forming groups, on the other on the relative disposition of these groups within the molecule. Generalizations are not easily made, but this much can be said for the azo dyes at least, that by increasing the number of chromophore and salt-forming groups, or by increasing the size of the molecule, the shade passes successively from yellow to orange, red, violet, blue, green, and black.

Azo Dyes

Azo dyes contain at least one diazo[2] group, the divalent chromophore $- N = N -$ combined with two aromatic radicals. The simplest chromogen in this class is azobenzene, which has weak coloring power; on introduction of salt-forming groups, the coloring power increases.

The main method[3] of formation of diazo substances is by the "diazotization" of primary amines, followed by "coupling." Diazotization takes place when nitrous acid, HNO$_2$, reacts on the primary amine group,

* In collaboration with Robert Kuoch, Ph.D. (Basel), Consulting Chemist for Dyes, of Buffalo, N. Y.

[1] The hydroxyl and carboxyl form a sodium salt with caustic soda or soda ash, while the amino group forms a hydrochloride with hydrochloric acid.

[2] Diazo means two nitrogens, from azote, the French word for Nitrogen. Diazo is contracted to azo, so that this latter expression also means two nitrogens in the form of $- N = N -$.

[3] Other methods are the reduction of nitro derivatives, and the action of a nitroso body on a primary amine.

NH_2, attached to the benzene, naphthalene, or certain other nuclei, in the presence of hydrochloric acid. Inasmuch as nitrous acid is unstable, its sodium salt, $NaNO_2$, is used, with an extra amount of hydrochloric acid.

$$C_6H_5.NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5-N{=}N-Cl + NaCl + 2H_2O$$
<div align="center">

benzene diazonium
chloride
</div>
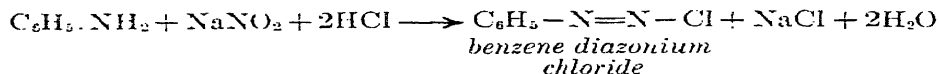
Examples of coupling reactions with benzene diazonium chloride:

phenol

aniline

α-naphthylamine

-naphthol
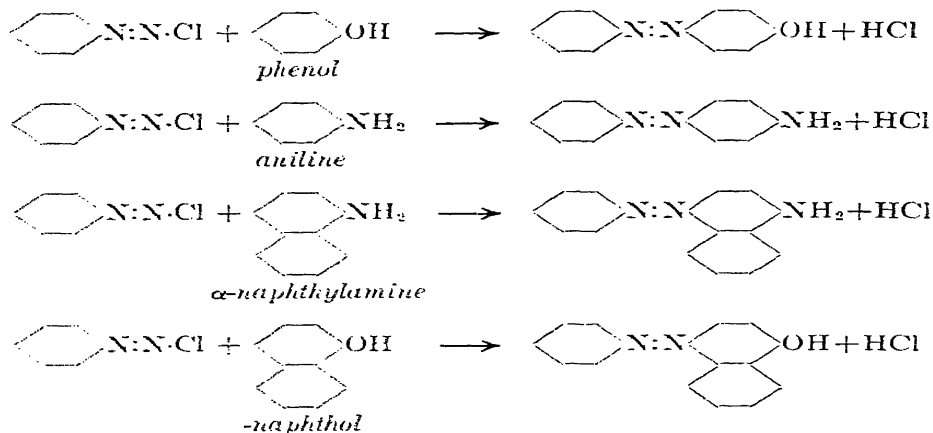
It will be noticed that the compounds with which the diazonium chloride reacts contain the salt-forming groups of OH or NH_2. It is this property, possessed by the diazonium grouping, of combining with aromatic compounds containing one of these two salt-forming groups, which renders possible the formation of the numerous azo dyes. Certain general considerations may well precede the reactions for dye formation.

The diazo group does not enter at random, but in certain definite positions. The attack is generally in the nucleus, and one molecule of hydrogen chloride is eliminated. For the benzene derivatives, the attack is on the hydrogen para to the salt-forming group, or if that is occupied, in the ortho position; never in the meta position. Coupling in alkaline solution is rapid; in acid solution, slow. The alkaline solution must be used for phenol and substituted phenols, in order to form a solution; they are not soluble in water. The acid solution must be used for aniline and other amines, again in order to bring them in solution. The alkaline solution removes the hydrogen chloride generated by the reaction as fast as it is formed. In the acid solution, such removal does not take place, unless sodium acetate is added, as is usually done; it is customary to hasten the reaction near the end by adding some soda ash.

In the naphthalene derivatives, the orientation of the entering group is somewhat different. In α-naphthol, the attack is at 4, or para; if 4 is occupied, the diazo group enters at 2, or ortho; this is in agreement with the rule for benzene derivatives, hence it may be considered normal.

In β-naphthol, the coupling takes place at **1**; never at **3** and never at **4**. The naphthols are coupled in alkaline solution.

α-naphthol   *β-naphthol*
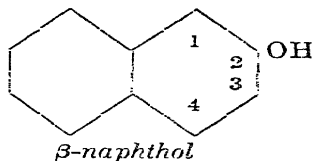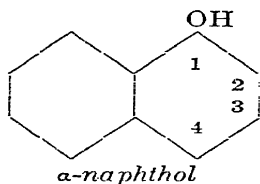
The same position is taken by the diazo group when NH_2 replaces the hydroxyls; the substance is then a naphthyl amine, and the coupling is performed in acid solution.

The sulfonic group, SO_3H, is also a salt-forming group, but it does not have the power, when alone, to cause coupling. In the naphthalene derivatives the presence of the sulfonic group influences in some cases the place of entry of the diazo group.

The carboxyl group, COOH, is also a salt-forming group: except in a few cases of no commercial importance, it does not cause coupling when alone.

Certain aminonaphthol sulfonic acids couple twice, and in this case, the place of entry depends upon whether the coupling is performed in acid or alkaline solution. If acid, the coupling is ortho to the amino group; if alkaline, ortho to the hydroxyl. In the three samples following, the place of entry for acid coupling is marked X; for alkaline coupling, Z.
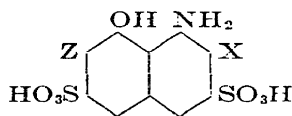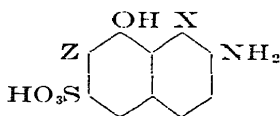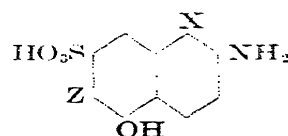
H acid[4]   *Gamma acid*   *J acid*

For these intermediates, too, alkaline coupling is rapid, acid coupling slow.

Ortho- and para-diamines in both the benzene and naphthalene series do not couple at all, only the meta-diamines do.
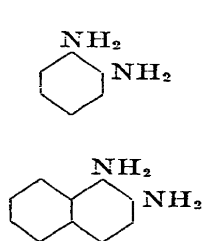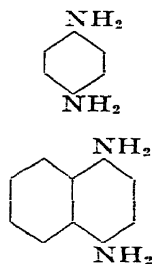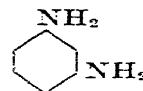
ortho-diamines   *para-diamines*   *meta-diamine*

[4] It is recommended that the reader enter the formulas and names of the more important intermediates on a 5″ x 8″ card, and that he place this card next to the book while reading this chapter.

The procedure for diazotizing is to add at a slow rate a measured solution of sodium nitrite to the acid solution of the primary amine, in a wooden vat provided with an agitator. By means of direct ice addition, the temperature is maintained low, usually 0° to 5° C.; generally a solution results. The diazonium compound is not isolated, but the solution is run at once at a slow rate into the alkaline (or acid) solution of the intermediate with which the diazonium compound is to be coupled. After the addition of the diazonium compound, the batch is agitated for a period varying between 8 and 72 hours, until coupling is complete. The solution of the dye is then warmed, solid salt (NaCl) is added and allowed to dissolve; on cooling the dye separates out and is filtered in a plate and frame press. The apparatus is illustrated further, under benzidine.

Many of the compounds named in this chapter are described in the previous one and may be looked up there; the formulas of others are given at the proper place. It will be remembered that each corner of the benzene hexagon represents CH; where coupling has taken place, the hydrogen has been lost in the formation of hydrogen chloride, and its place taken by the diazo group. The full formula of the first azo dye, Butter Yellow, given in the next division, is therefore
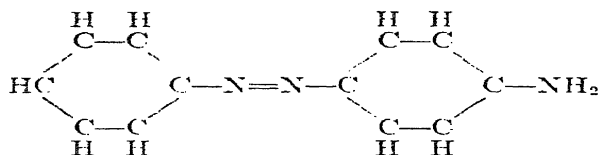
Mono-Azo Dyes. The mono-azo dyes contain the group $-N=N-$ once; the simplest example is aminoazobenzene, "butter yellow", soluble in oil and in butter; its use as a textile dye is unimportant. It is made by coupling diazonium chloride with aniline in acid solution [5]

Butter Yellow
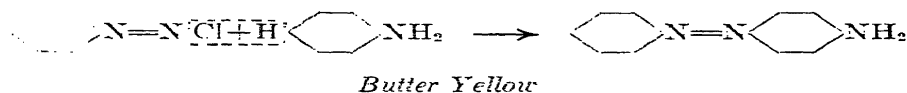
On sulfonating it with fuming sulfuric acid, Fast Yellow is formed, which is a mixture of the mono- and di-sulfonic derivatives:

Fast Yellow
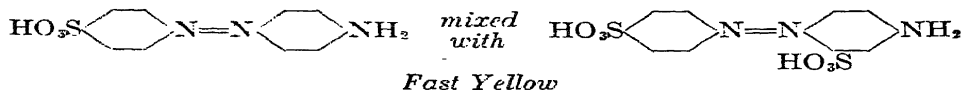
[5] An intermediate step is omitted; there is first formed diazoaminobenzene ⟨ ⟩ $-N=N-NH-$ ⟨ ⟩ and this rearranges itself under the influence of the acid into aminoazobenzene ⟨ ⟩ $-N=N-$ ⟨ ⟩ HN_2. This intermediate compound is formed in every coupling reaction involving an amine.

Diazonium chloride coupled (acid) with meta-phenylene diamine gives Chrysoidine, which dyes a brown-yellow. The diazonium chloride, it will be remembered, is made by diazotizing aniline.

Chrysoidine
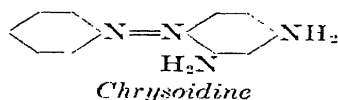
Sulfanilic acid
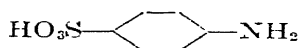
diazotized gives *p*-sulfonic diazonium chloride which may be coupled (alkaline) with α-naphthol to form Orange I.

α-naphthol → *Orange I*
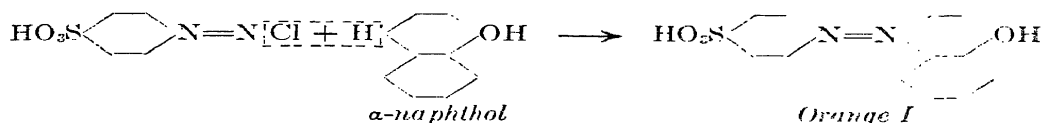
If instead of α-naphthol, diphenylamine is used, Orange IV results. Metanil Yellow is an isomer of Orange IV: it is made in the same way, except that *m*-sulfonic aniline is the body which is diazotized.

Orange IV   *Metanil Yellow*
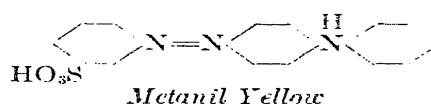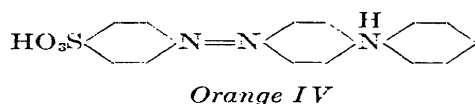
If sulfanilic acid is diazotized and coupled with dimethyl aniline, Methyl Orange or Helianthine is obtained.

para-sulfonic diazonium chloride (from sulfanilic acid)   *dimethyl aniline*   *Methyl Orange*
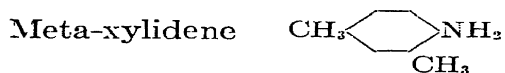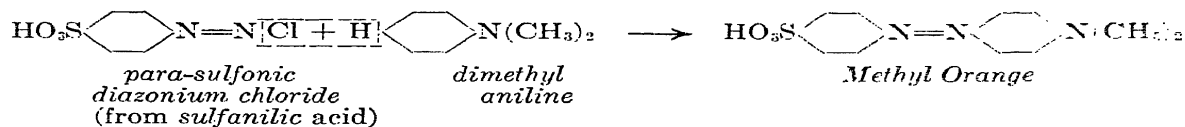
Meta-xylidene   diazotized gives the corresponding

dimethyl-benzene-diazonium chloride; if the solution is run into an alkaline solution of R acid, Ponceau R, a wine-red dye, results. To avoid writing formulas twice, only the formula of the dye will be given, but the place of entry will be marked by an asterisk; this will make it easy to recognize the component parts of the dye. It will be understood that a molecule of HCl was formed and removed at the place marked *. Bordeaux B, which dyes a purer red, consists of diazotized α-naphthylamine coupled (alkaline) with R acid.
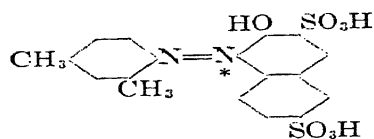
Ponceau R
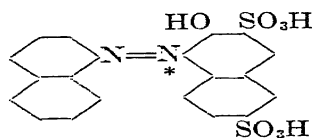
Bordeaux B

Azo Rubine is made from diazotized naphthionic acid, coupled (alkaline) with Nevile and Winther's acid. Amaranth contains naphthionic acid again, but this time coupled (alkaline) with R acid
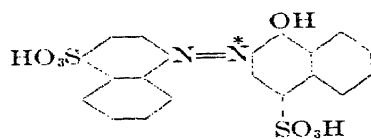
Fast Red C
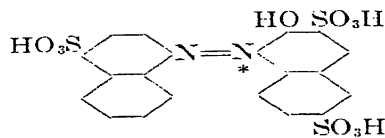
Amaranth

Chromotrope 2R consists of diazotized aniline coupled with chromotropic acid, while Chromotrope 6B is *p*-aminoacetanilide coupled with the same chromotropic acid.
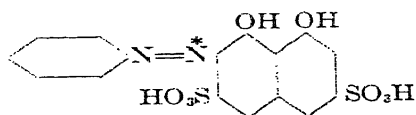
Chromotrope 2R
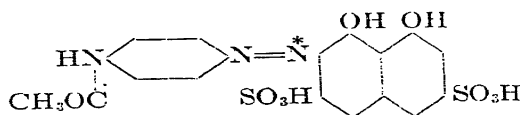
Chromotrope 6B

Secondary Dis-Azo Dyes. If an azo dye has been made with an intermediate which contains a free primary group, this group may be diazotized by treating the azo dye with sodium nitrite solution and hydrochloric acid; the resulting diazonium compound may then be coupled to a new intermediate, and a dye will result which contains two azo groups. Such a dye is a dis-azo dye, and, when prepared in this way, it is a secondary dis-azo dye. Primary dis-azo dyes are described later, under benzidine dyes.

Several examples will be given.

Para-aminoazobenzene or "butter yellow" is again the simplest case; it may be diazotized, and if then coupled with R acid, Cloth Red 2R is formed:

Diazotized
para-aminoazobenzene   *R acid*   *Cloth Red 2R*
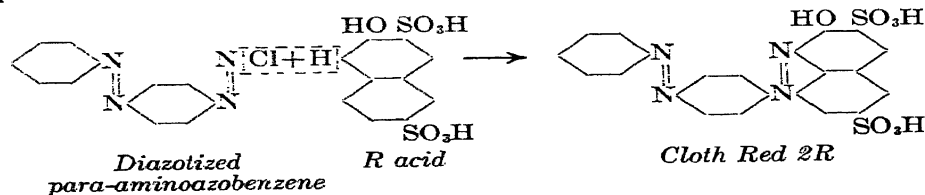
If the diazotized para-aminoazobenzene is coupled with G acid, Brilliant Crocein M results. Amino-azotoluene may be diazotized and if this is coupled (alkaline) with R acid, Cloth Red B is obtained.
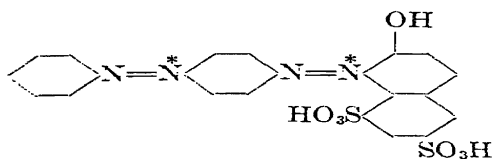
Brilliant Crocein M
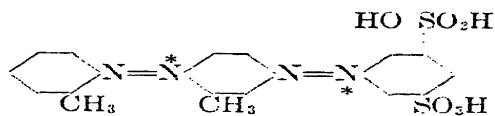
Cloth Red B

In the manufacture of Fast Black L, para-aminosalicylic acid is diazotized and coupled with α-naphthyl amine; the resulting compound, containing one azo ($-N=N-$) group, is diazotized again, and then coupled with Gamma acid.

para-aminosalicylic acid (diazotized)   and   *α-naphthylamine*
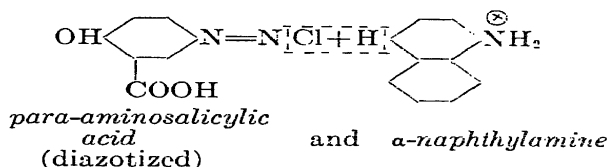
give a first dye. This first dye treated with sodium nitrite and acid gives the diazotized product (the new azo group forms at ⊘) the solution of which is poured into the alkaline solution of γ-acid.

Fast Black L
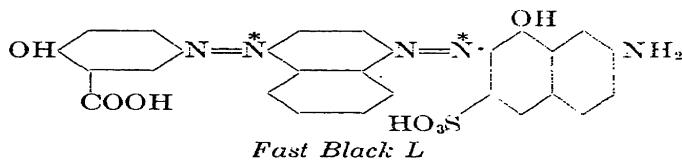
Sulfanilic acid diazotized and coupled with α-naphthylamine gives a mono-azo product which has a free amino group; this may be diazotized in turn and if coupled with 1-amino-8-naphthol-3: 6-disulfonic acid (H acid), the black dye called Buffalo Black 10B results. Another black in this class is Durol Black.

Buffalo Black 10B

Durol Black
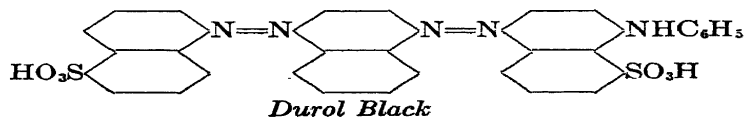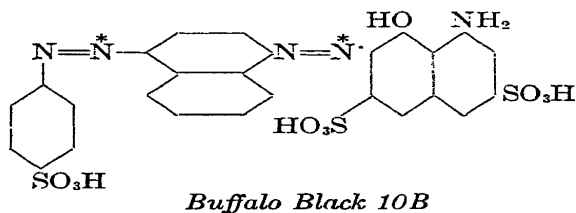
It will be observed that for these black dyes the molecule is large, and that it contains in each case the grouping

$$-N=N-\left\langle\right\rangle-N=N-$$

Mordant Azo Dyes. Certain azo dyes have the property of forming insoluble "lakes" with metallic oxides; these lakes are fast to washing. The metallic oxides chiefly used are those of chromium and copper. The observation has been made that in order to form lakes, there must be present in the molecule a hydroxyl (OH) group with either a second hydroxyl, a carboxyl (COOH) or an azo $(-N=N-)$ group in the ortho position to the hydroxyl; this observation is called a rule, and has already been given in a previous chapter. The following dyes are examples of such lake-forming azo dyes.

Para-nitraniline diazotized and coupled (alkaline) with salicylic acid forms the so-called Alizarine Yellow, one of the simpler of the mordant azo dyes.

$$NO_2\left\langle\right\rangle N=N\left\langle\right\rangle OH$$
$$COOH$$

Alizarine Yellow
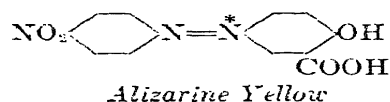
Another example is Chrome Brown, made by diazotizing picramic acid and coupling it (acid) with *m*-toluenediamine:

picramine   *Chrome Brown*
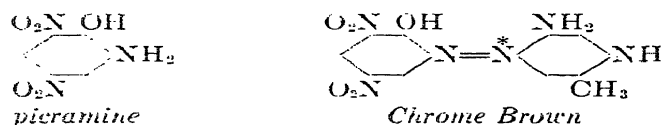
Still another example is Chrome Black P V, shown below; it is made by diazotizing ortho-aminophenol-para-sulfonic acid and coupling it (alkaline) with 1,5 dioxynaphthalene. Two other important members of this group are Acid Alizarine Black and Palatine Chrome Black, whose component parts are sufficiently shown in the formulas:

Chrome Black PV   *Acid Alizarine Black*   *Palatine Chrome Black*
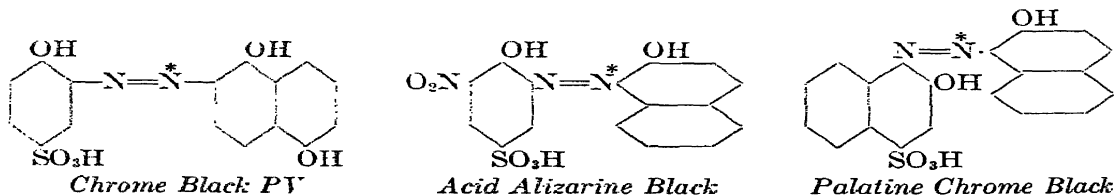
Diamond Black F is a secondary dis-azo dye which is also a mordant azo dye; it contains salicylic acid, α-naphthylamine, and Nevile and Winther's acid.
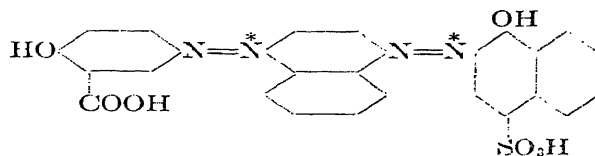
Diamond Black F

It will be noted that this dye has two lake-forming groupings.

Primary Dis-Azo Dyes. The azo dyes described in the previous divisions are mainly direct dyes for wool, or in the last division, mordant dyes for wool. The primary dis-azo dyes in the present division are mainly direct dyes for cotton, to which they are applied in the form of their sodium salt, which is also the form in which they are manufactured and shipped. Such dyes are dis-azo, since they contain two azo groups; and they are called primary, because the substance forming the starting point contains two primary amine (NH_2) groups; both may be diazotized, and both resulting diazonium groups may be coupled to some intermediate. Benzidine or closely related substances are used for these dyes.
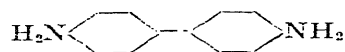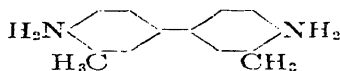
benzidine　　　　　　　　*tolidine*　　　　　　　　*dianisidine*

In addition to the primary dis-azo dyes there are tris-azo and tetra-azo dyes which are direct dyes for cotton.

Both amino groups in benzidine may be diazotized simultaneously without being even partly destroyed by the nitrous acid, and without needing to be protected by acetylation. This property is shared by other substances among which diaminostilbene-disulfonic acid and diamino-diphenylurea derivatives are of importance.[6] The simultaneous diazotization of two amino groups is called tetrazotization, and the resulting product a tetrazo compound.[7]

diaminostilbene　　　　　　　　　　*diaminodiphenylurea*
disulfonic acid

Benzidine in the free state is a brownish powder insoluble in water but soluble in dilute hydrochloric acid; both amino groups are diazotized together, and the resulting solution poured into the alkaline intermediate; if the same intermediate is to be introduced at each azo group, two mols

[6] Toluene diamine para-sulfonic acid may be diazotized at both groups without covering.
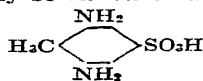
[7] Para-phenylenediamine H_2N.⟨ ⟩.NH_2 cannot be diazotized at both groups without destruction.

are used. The commercial procedure may be illustrated for Direct Blue 2B, which is made by coupling benzidine with two molecules of H acid.

$$H_2N\langle\_\_\_\rangle\text{---}\langle\_\_\_\rangle NH_2 \qquad ClN{=}N\langle\_\_\_\rangle\text{---}\langle\_\_\_\rangle N{=}NCl$$

benzidine *tetrazotized benzidine*
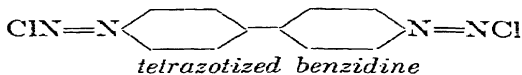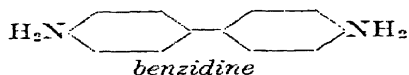
Benzidine is suspended in water in a wooden vat (Fig. 169), five mols [s] of hydrochloric acid are added, and the whole brought to a boil by passing in live steam. The required amount of acid is four mols, as indicated by the diazotizing reaction in the introduction to this chapter, two mols for each amino group; one mol is then the excess used.
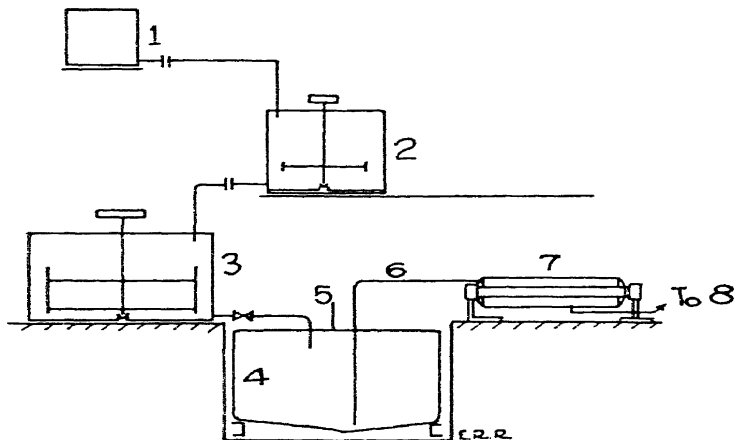
FIGURE 169.—Apparatus for manufacturing a benzidine dye; 1, sodium nitrite solution; 2, vat for tetrazotizing the benzidine hydrochloride; 3, vat for coupling; it contains the alkaline solution of H acid. to which contents of 2 are added; 4, blow-case; 5, compressed air; 6, discharge line to press; 7, press; 8, vacuum drier.

As soon as solution has taken place, ice is added, when a large part of the benzidine hydrochloride separates in a finely divided solid. Two mols of sodium nitrite, in solution in vat 1, are run in gradually; for 184 pounds of benzidine (one mol) the addition of 138 pounds of nitrite (two mols) would require two hours. In the meantime 446 pounds (two mols) of H acid are dissolved in an excess of soda ash in water (vat 3); to this, the contents of 2 are added, while stirring. Enough ice is added to keep the temperature at 5° C. The dye separates out only in part; in order to separate it all, the contents of the vat are warmed by passing in steam through a movable pipe, solid salt is added and dissolved, then the contents cooled; all of the dye precipitates. The soda ash used with the H acid is sufficient to form the sodium salt of the dye.

The suspension is run into a wooden or an iron plate and frame filter press [9]; the filtrate is tested with more salt, and if exhausted, it is run to the sewer. The cake is not washed, but merely freed from most of the adhering mother liquor by blowing with compressed air, while still in the press; the portion of the liquor retained must be removed by drying. The

[s] The mol is the number of grams or pounds numerically equal to the molecular weight.
[9] Chapter 42.

moist cake is discharged onto shallow trays which are placed in a stationary vacuum drier wherein the moisture is removed at moderate temperature (70° C.). The trays are placed each on a hollow steel shelf in which low-pressure steam or hot water is circulated. All dyes discussed in this chapter are solids, and are sold in the form of powders, or pastes.

Direct Blue 2B
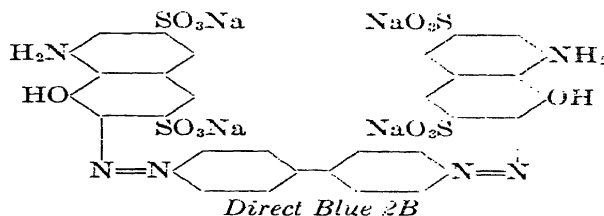
If it is desired to couple different intermediates at the two azo groups, it is possible to do so because one group couples fast while the other couples slowly. By pouring one mol of the intermediate into the tetrazonium solution (the reverse of the usual order), one of the diazonium groups is coupled in each molecule; the second remains free,[10] and may be coupled in a second operation. In such a case one vat for each intermediate must be provided, and must be placed at a higher level than the benzidine vat.

Direct Blue 3B is one shade bluer than the previous dye, and consists of tolidine coupled twice (alkaline) with H acid.

Sky Blue FF is dianisidine tetrazotized and coupled twice (alkaline) with S S acid,[11] Direct Blue N R contains tetrazotized benzidine coupled once (alkaline) with H acid, which has previously been coupled to diazotized aniline, and once with γ-acid (alkaline).

Sky Blue FF

Direct Blue NR
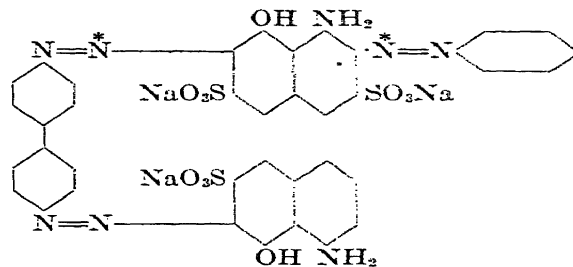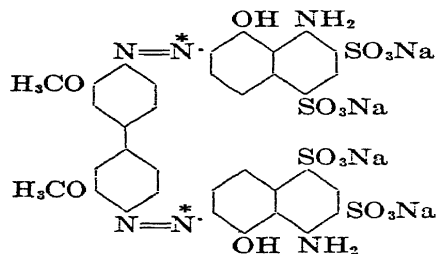
A green dye is made by coupling tetrazotized benzidine with H acid (alkaline) which has previously been coupled (acid) with diazotized para-nitraniline, and at the second diazonium group with phenol.

[10] The end-point for the first group is found by touching drops of the solution on a filter paper wetted with an alkaline solution of R acid.
[11] 1-amino 2-, 4-disulfonic 8-hydroxynaphthalene.

OH NH₂

N=N OH NH₂ N=N NO
NaO₃S SO₃Na

N=N OH

Direct Green
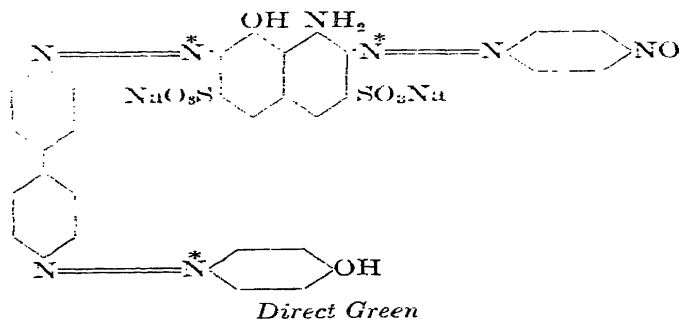
The composition of two orange dyes, two red dyes, a violet dye, and a black dye (these latter two on page 495) are exhibited by their formulas:

NH₂ CH₃
H₃C N : N
NH₂ SO₃H

N=N NH₂
HO₃S NH₂
NO₂

H₃C NH₂ CH₃
N : N
NH₂ SO₃H

NO₂
HO₃S NH₂
N=N NH₂

Toluylene Orange R   *Pyramine Orange R*

OH
N : N
HO₃S

N : N OH
COOH

OH
N : N
HO₃S

HO₃S NH₂
N : N
O
H

Bordeaux (red)   *Direct Red J*
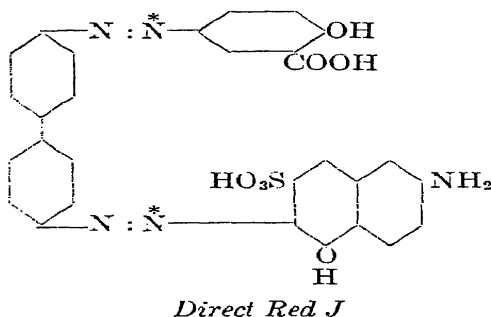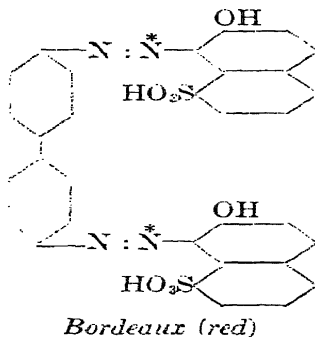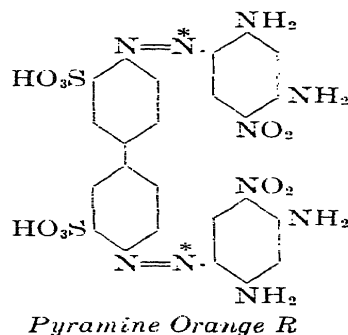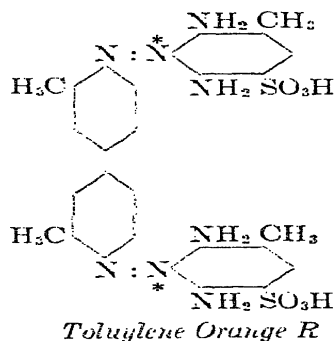
In Direct Violet, the γ-acid is coupled acid, as the place of entry of the azo groups indicates; the coupling may be performed alkaline, when the place of entry will be adjacent to the hydroxyl group (at X X), and this slight difference in structure causes a blue dye to be produced, instead of a violet.

Stable Diazo Salts. A new development which is rapidly gaining favor is the manufacture of stable diazo salts, which consist of the uncoupled diazonium compounds in the form of its zinc, magnesium or tin salts. After forming the salt, the salted-out material is filtered and
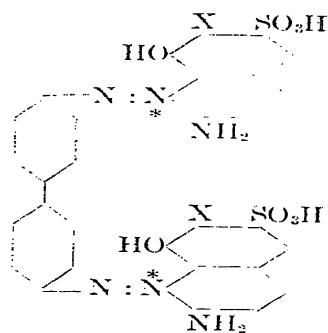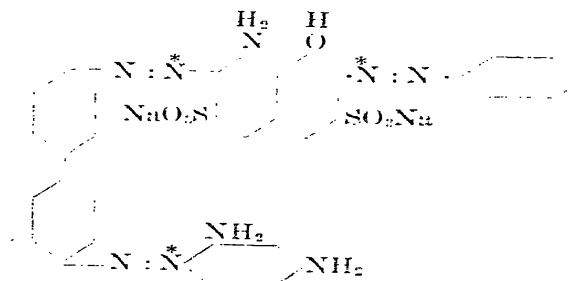
Direct Violet   *Direct Black*

dried as thoroughly as possible on a suction nutsch. Next the cake is discharged and mixed with anhydrous potassium alum, or anhydrous magnesium sulfate, which take up the remaining water in the form of crystal water. This is done because the diazo salt cannot be dried by heating, since it would be likely to explode. The dry diazo salt is shipped to the customer, who places it in water solution, and passes cotton skeins or cloth through it. The goods are wrung out, and sent through an alkaline naphthol (or other) bath, so that coupling takes place on the cloth. The result is a light-fast dye.

It will be noted that the process resembles vat dyeing: it requires much simpler formulas, fewer chemicals, less skill, and less time.

The diazo compound is stable by virtue of the formation of its salts; hence the name.

Dye for Gasoline. In order to color gasoline red, a dye called Oil Red EG is used, among others. Its formula will indicate that it is made by diazotizing aminoazoxylene, and coupling it with β-naphthol.
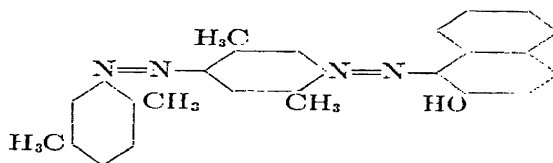
Oil Red EG

STILBENE DYES

The stilbene dyes contain the chromophore — N:N — , not obtained however by diazotization of amines, but by the action of caustic soda on para-nitro-toluene sulfonic acid. The colors formed by this reaction vary with the length of heating, temperature and concentration of caustic, so that in order to duplicate a color, the exact conditions must be observed. Little is known of the constitution of such dyes, and most of the brands on the market consist of mixtures of products formed during the reaction.

The Mikado dyes belong to this group; Sun Yellow, shown below, is an example.
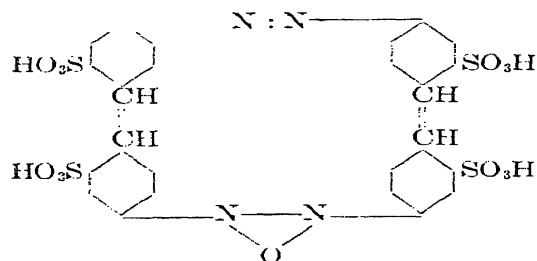
Sun Yellow

Another example of the stilbene dyes is Brilliant Yellow (used chiefly for tinting paper); its formula is given below. Treated with ethyl chloride (C_2H_5Cl) under pressure, the two hydroxyls are changed to the ether groups (OH becomes OC_2H_5), and the more important Chrysophenine, a bright yellow dye which is faster than Brilliant Yellow, is produced.
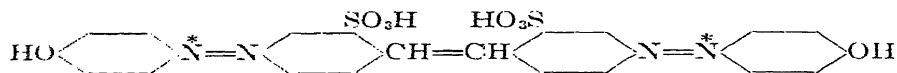
Brilliant Yellow

PYRAZOLONE DYES

The pyrazolone dyes contain the pyrazolone [12] nucleus
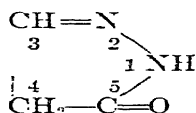
Tartrazine, a favorite yellow dye, will be the example for this group. It is made by mixing a solution of 1 mol dioxy-tartaric acid [13] and a solution of 2 mols phenylhydrazinesulfonic acid; on heating slowly, the dye forms.

Pyrazolone derivatives made from ethyl aceto-acetate condensed with phenyl hydrazine, para-sulfonic phenyl hydrazine, 3-6-dichlor-4-sulfo-phenyl hydrazine, and others, coupled with diazonium compounds of the benzene series, yield light-fast, clear yellows for wool. Coupled with a diazonium compound of the naphthalene series, a chromed red is formed; coupling takes place at 4.

[12] 1-phenyl-3-methyl-pyrozolone is antipyrine, a pharmaceutical.
[13] Made by oxidizing tartaric acid with nitric acid.

COOH
C=N
N · C$_6$H$_4$SO$_3$H
C=C · OH
N
N · C$_6$H$_4$SO$_3$H

Tartrazine
(*a yellow*)

CH$_3$
C=N
N ·
C=C · OH
N
N
HO
SO$_3$H

Eriochrome Red B
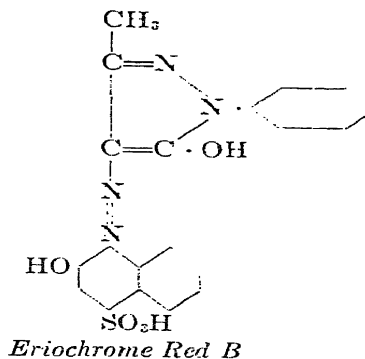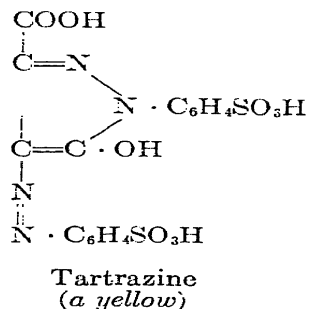
Triphenylmethane Dyes

Rosaniline, fuchsine, malachite green, and crystal violet are members of this class; its chromogen has three benzene nuclei attached to a central carbon, the so-called methane carbon, but one of the benzene structures has been altered to the quinone structure. The salt-forming groups are para to the methane carbon, and are usually the amino groups. Para-fuchsine, or Fuchsine, is the simplest triphenylmethane dye; it is a hydrochloride; the chromogen is shown next to it.

H$_2$N⟨⟩—C=⟨⟩=NH . HCl
NH$_2$

Fuchsine
(red)

H
⟨⟩—C—⟨⟩

Chromogen
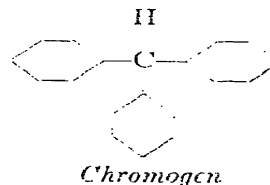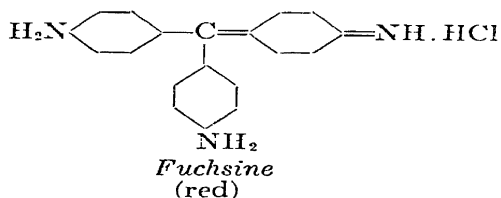
Fuchsine is the salt of a weak base; it is easily changed by alkali to the colorless carbinol. This property has greatly restricted its use; but if chlorine is present in the molecule, ortho to the methane carbon, the new dye is alkali resisting. As example, Fast Green is given.

(CH$_3$)$_2$N⟨⟩—C=⟨⟩=N(CH$_3$)$_2$. Cl
Cl

Fast Green
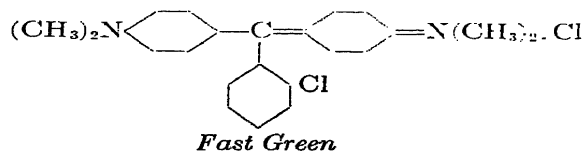
There are two methods of manufacture; one may be illustrated by rosaniline, which is made by condensing 1 mol each of aniline, para-toluidine and ortho-toluidine in the presence of nitrobenzene as oxidizer. On neutralizing the resulting carbinol with hydrochloric acid, the dye forms.

$$H_2N-\!\!\!\!\!\!\bigcirc\!\!-CH_3 \;+\; H-\!\!\!\bigcirc\!\!-NH_2 \;+\; H-\!\!\!\bigcirc\!\!-NH_2 \xrightarrow{+O_2}$$

leuco base → *Rosaniline* $+2H_2O$; $\xrightarrow{HCl}$ $+H_2O$
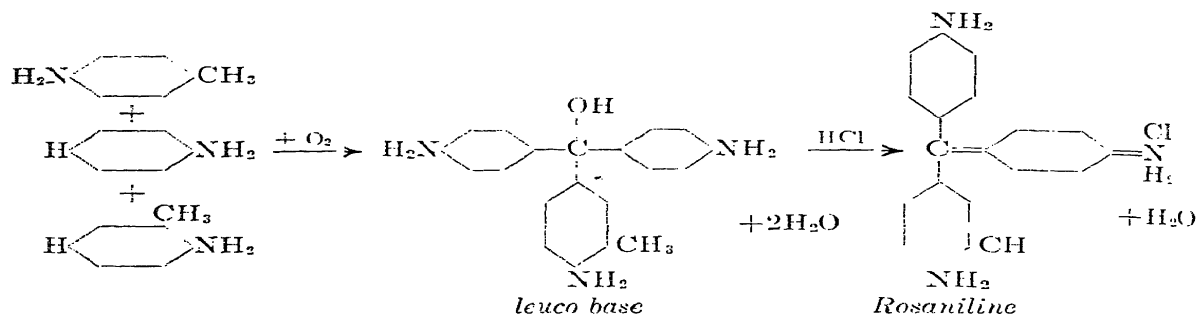
The other method involves the condensation of aromatic aldehydes, such as benzaldehyde, $C_6H_5.CHO$; monochlorobenzaldehyde, $Cl.C_6H_4.CHO$; and of ketones, such as Michler's ketone, $(CH_3)_2N.C_6H_4.CO.C_6H_4.N(CH_3)_2$, (made by passing phosgene, $COCl_2$, into dimethylaniline, $C_6H_5.N(CH_3)_2$) with aromatic bases. Benzaldehyde (1 mol) condenses with 2 mols dimethyl-aniline in the presence of zinc chloride to form a leuco base which on oxidation with lead peroxide and treatment with hydrochloric acid yields Malachite Green.

Malachite Green — $=N(CH_3)_2Cl$; $N(CH_3)_2$
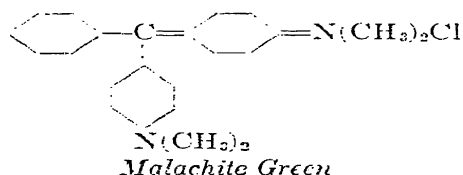
The condensation of ortho-chlorobenzaldehyde with dimethylaniline leads to Fast Green, with the formula as given above. Michler's ketone condenses in the presence of phosphorus pentachloride with dimethylaniline to a carbinol which is changed by hydrochloric acid to Crystal Violet. The same ketone condensed with a substituted α-naphthylamine gives Victoria Blue.

Crystal Violet — $(CH_3)_2N$ ... $=N(CH_3)_2$ Cl ; $N(CH_3)_2$

Victoria Blue — $(CH_3)_2N$ ... $=N(CH_3)_2$ Cl ; $H_5C_6.HN$
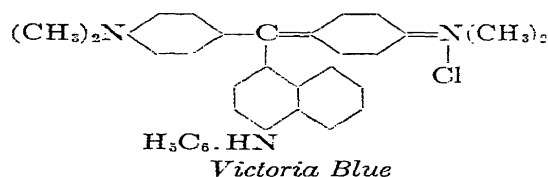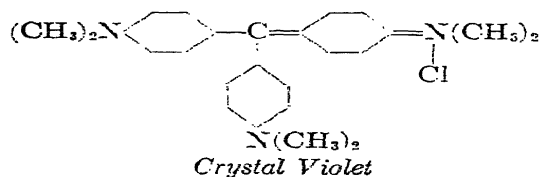
The diphenylmethane dyes are unimportant, except for Auramine, a yellow dye.

Auramine — $(CH_3)_2N-\!\!\!\bigcirc\!\!-C-\!\!\!\bigcirc\!\!-N(CH_3)_2$; $NH.HCl$
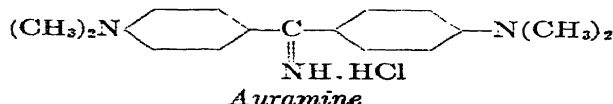
XANTHENE DYES

Fluorescein, eosine, and rhodamine represent each a series of dyes which contain the same central structure, called xanthene, with the formula
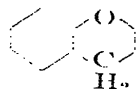
they are therefore classed together as xanthene dyes. Fluorescein is made by heating in an iron vessel phthalic anhydride (1 mol), resorcinol (2 mols), and zinc chloride; the temperature is regulated by means of an oil or metal bath and kept at 220° C. for 7 hours. The melt is dissolved in caustic soda, and the fluorescein precipitated by acidifying; it is a yellow-red powder. Its alkaline solution fluoresces green-yellow. Fluorescein itself is not an important dye.
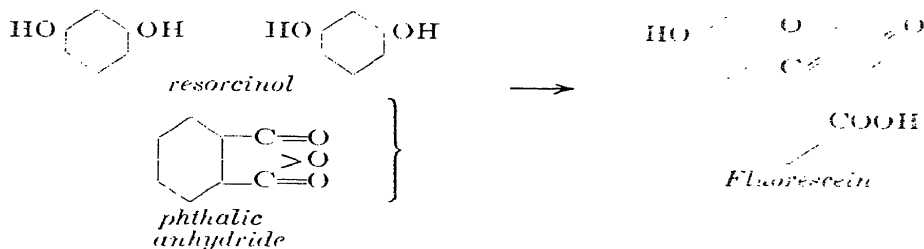
Dissolved in alcohol and treated with bromine while warm, four equivalents are absorbed to form tetrabromofluorescein or eosine.

Eosine (red)   Rhodamine B
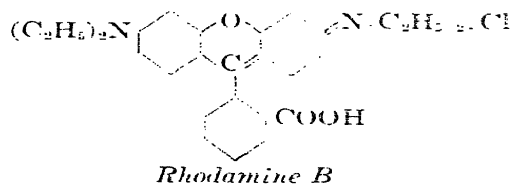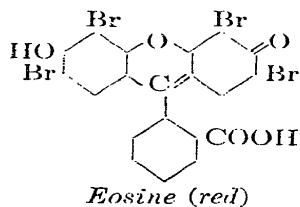
A number of other eosines are obtained by making dinitrodibromofluorescein, and similar compounds, or their esters.

Erythrosine is a di- or tetraiodofluorescein; Phloxine the tetrabromdichlorofluorescein.

Rhodamines are made by condensing phthalic anhydride with methylated or ethylated meta-aminophenols in the presence of zinc chloride and treating with hydrochloric acid. Rhodamine B, a bluish-red dye, is shown above.

Galleine is a good mordant dye for cotton; it is made by condensing phthalic anhydride (1 mol) with pyrogallol, 1,2,3-trihydroxybenzene (2 mols).

Related to the xanthene dyes are the acridines, azines, oxazines and thiazines. Acridine Yellow results from the condensation of meta-tolu-lene-diamine with formaldehyde followed by oxidation and treatment with hydrochloric acid. Phosphine is a by-product of the manufacture of fuchsine, and is an acridine dye.
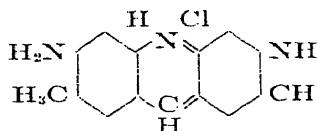
Acridine Yellow
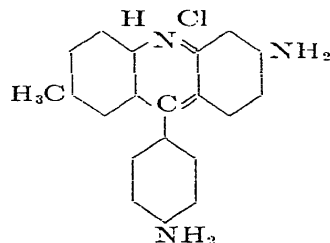
Phosphine

The quinone-imide dyes, derivatives of indamine and indophenols, have not been listed separately because in themselves they are not important; but they require mention here because azine dyes are made from them. Indamine is made from para-phenylenediamine and aniline; Safranine is an azine dye. The azine nucleus has two nitrogen atoms in the central ring.

p-phenylene-diamine   *aniline*   *indamine (solid)*
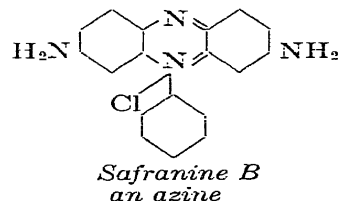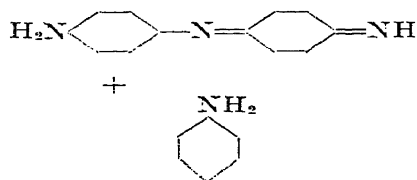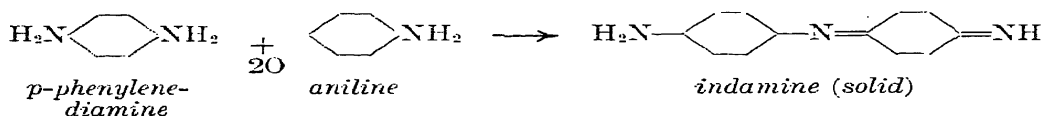
Safranine B
an azine
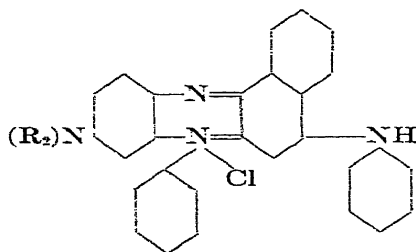
Wool Fast Blue GL and BL   *Safranine*
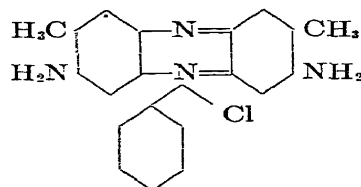
Methylene Blue is a thiazine; its nucleus contains nitrogen and sulfur in its central part:
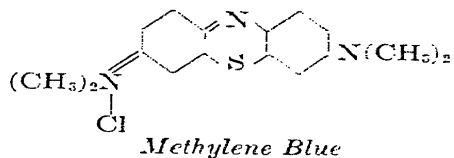
Methylene Blue

On nitrating Methylene Blue, Methylene Green is formed. Meldola's Blue is an oxazine dye.

ALIZARINE DYES

The alizarine dyes may be considered derivatives of anthraquinone; they are actually made from anthraquinone in many cases, but some of them (for example Anthrarufin) are made by condensing benzene derivatives. The anthraquinone is the chromogen, which contains two chromophore groups, the two $> C = O$ groups; on introducing the salt-forming group OH, a dye results. With two hydroxyls at 1 and 2 (consult Chapter 27 for the numbering), the dye is Alizarine proper, a mordant dye insoluble in water; if sulfonic groups are introduced besides, the dye becomes soluble, and is an acid dye. Alizarine is valuable as a dye in itself, but it is still more so as the starting point of a large number of newer dyes of varied shades. (Formulas in Chapter 27.) The sodium salt of β-sulfonic anthraquinone is called silver salt.

Alizarine is made by heating under pressure 100 parts of silver salt, so called because it looks like powdered silver, 250 to 300 parts caustic soda, 10 to 15 parts potassium chlorate, and some water, to 180° C. in a closed cast-iron or steel vessel provided with a slow-moving agitator. The operation is an alkaline fusion, discussed in the previous chapter; but the hydroxyl groups introduced number one more than the sulfonic acid groups present. The resulting melt is dissolved in water, acidified, and the precipitated alizarine filtered and washed. It is sold in the form of a 20 per cent paste; it is used with mordants.

On sulfonating Alizarine, Alizarine Red is formed, a mixture of the mono- and disulfonic derivatives; this is now an acid dye.

Alizarine Orange is 3-nitro-alizarine; while Alizarine Brown is 4-nitro-alizarine, and when this nitro group is reduced, the dye formed is Alizarine Garnet (German Grenat).

Alizarine Blue is made from Alizarine Orange, β-amino alizarine, glycerine and sulfuric acid.[14] Other alizarine dyes are Anthracene Brown, 1.2,3-trioxyanthraquinone, Purpurine 1,2,4-, Flavopurpurine 1,2,6-, and

Alizarine Maroon
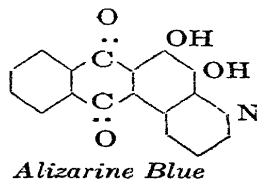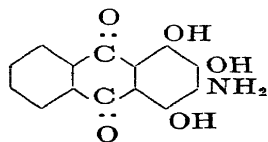
Alizarine Blue

[14] The Skraup synthesis.

Oxyanthrarufine 1,2,5-trioxyanthraquinone. Alizarine Bordeaux is 1,2,5,8-tetraoxyanthraquinone. All these hydroxyl groups need not be introduced by alkaline fusion, for sulfonating with oleum of certain strength in the absence or presence of boric acid or other substance, and subsequent water treatment, permits the introduction of the hydroxyl group and a control of its place of entry.

VAT DYES

A vat dye is insoluble in water, dilute acid or alkali; it must be reduced to the so-called leuco compound in order to be soluble, and it is only in this state that it has affinity for the fiber. The reduction was formerly done in a vat, hence the name, vat dyes. The reduction is performed with sodium hyposulfite,[15] a powerful reducer, or by zinc dust and sodium bisulfite; sodium sulfide reduces only partly. After application to the fiber, the original insoluble material reforms on exposure to the air by oxidation.

Three groups may be distinguished among the vat dyes: those which are derived (a) from Indigo itself, (b) from anthraquinone, and (c) other vat dyes which do not fit in a or b, such as Hydrone Blue.

(a) The indigo group: Artificial indigo was synthesized originally from anthranilic acid and chloroacetic acid, followed by several other operations; this procedure is now obsolete for indigo, but is still used for thio-indigo. The next procedure is simpler; aniline and chloroacetic gives phenyl glycine, and this condenses to indoxyl by fusion with alkali.

The really modern method is remarkably simple; it is a combination of two reactions described in the patent literature. The first step is the preparation of phenyl glycine. In a water solution of sodium bisulfite, formaldehyde is placed; to this is added aniline oil, and then sodium cyanide. The nitrile is formed in the cold, separated by filtration and washed free from the sulfite salt. The nitrile crystals are warmed in an alkaline slurry; ammonia is evolved, and a solution of the phenyl-glycine salt is formed.[16]

$$\left.\bigotimes\!NH_2 + \begin{matrix} NaHSO_3 \\ CHOH \\ NaCN \end{matrix}\right\} \longrightarrow \bigotimes\!.NH.CH_2.CN \quad ; \quad \bigotimes\!.NH.CH_2.COOH$$

nitrile of phenyl glycine   *phenyl glycine* (solid)
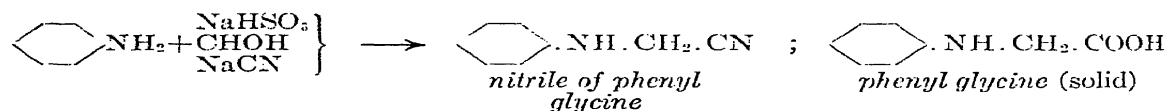
In the second step, the phenyl glycine salt is condensed by heating with a eutectic mixture of potassium and sodium hydroxide,[17] in the presence of sodamide,[18] which removes the water formed. The yield is excel-

[15] Chapter 4.

[16] German Patent 135,332, also 151,538.

[17] German Patent 137,955.

[18] Sodamide is made by passing dry ammonia gas over melted sodium in a closed vessel, hydrogen is formed, and is burned at a suitable outlet. $2Na + 2NH_3 = 2NaNH_2 + H_2$. Sodamide is a white solid melting at 120° C. German Patent 117,623. These four patents are reproduced in Friedlaender's collection (*see* reading references).

lent. mainly because the reaction temperature, 200° to 220° C., is much lower than in previous methods. The higher temperatures meant greater decomposition of the indoxyl.

potassium salt
of phenyl glycine
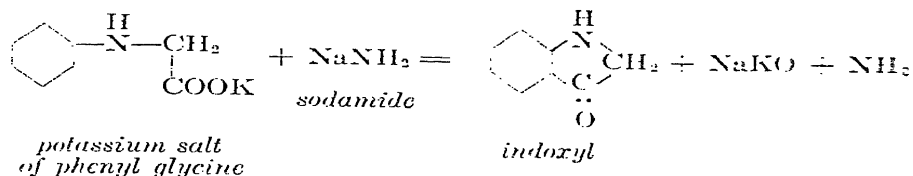
indoxyl

After the fusion, water is added, and in this alkaline solution, air is blown; the indoxyl is oxidized to indigo, which precipitates and is filtered off, washed, and dried. Two molecules of indoxyl form one of indigo with the removal of 4 hydrogen atoms (as water).

Hydroxyethylaniline, formed when ethylene chlorhydrin is treated with aniline, is synthesized commercially to indigo with a molten mixture of potassium and sodium hydroxides containing ground calcium oxide; hydrogen is evolved.

The thioindigos are made from phenyl thioglycine derivatives.

In order to apply indigo to fibers, it is reduced to indigo white, which is soluble in alkalies.

Indigo (blue)
(insoluble powder)

Indigo White
(soluble in alkali)

Thioindigo
bluish-red
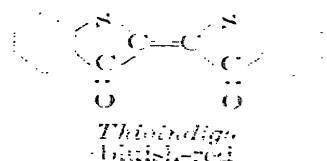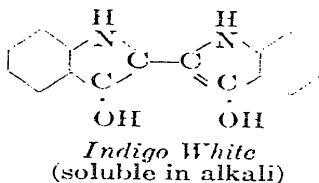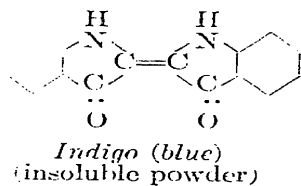
Of the halogen derivatives, known commercially as Brilliant Indigos, those containing bromine give increasing green shades, while the chlorindigos lie between indigo and bromindigo in brilliancy.

Bromindigos are prepared by the direct bromination of indigo with liquid bromine in a ball mill, or by refluxing in nitrobenzene.

The direct chlorination of indigo is performed in glacial acetic acid or nitrobenzene suspension, and is less simple.

Indigo is produced in the form of a 20 per cent paste, for domestic and export consumption. In 1930, 24,327,000 pounds of synthetic indigos were produced in the U. S.; in 1935, much less, 13,614,238 pounds.[18a]

(b) The anthraquinone vat dyes are made from α- or β-amino-anthraquinone; α-aminoanthraquinone may be made by direct nitration followed by reduction; β-aminoanthraquinone must be made by an indirect method; the β-sulfonic anthraquinone is treated with ammonia under pressure. The simplest of these dyes is Algol Yellow.

[18a] U. S. Tariff Commission, reports on Dyes.

$$O \quad NH.CO.C_6H_5$$

Algol Yellow
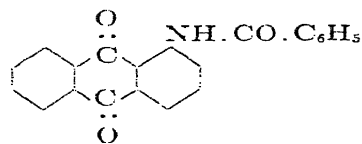
By fusing β-aminoanthraquinone with caustic potash, Indanthrene is formed. a beautiful blue vat dye which is the fastest dye known at present. To this class belong also Flavanthrene (yellow), Indanthrene Gold Orange, and the important phenanthrones.

β-aminoanthraquinone (2 mols)   *Indanthrene* (blue)
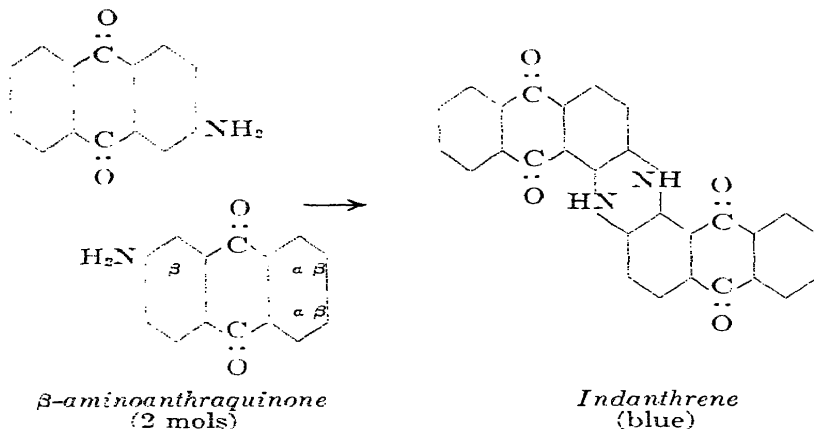
(c) Hydrone Blue is a class of sulfur dye which may be reduced by sodium hyposulfite $Na_2S_2O_4$ without destruction, unlike the typical sulfur dyes. In order to prepare Hydrone Blue R, para-nitrosophenol is condensed with carbazol in the presence of sulfuric acid at a definite temperature: the product is fused with alkali polysulfide. The formula of the dye is not fully known.

carbazol + *p-nitroso-phenol*   reduced ↓ (+2H)

Hydrone Blue R $\xleftarrow{\text{by sodium polysulfide}}$
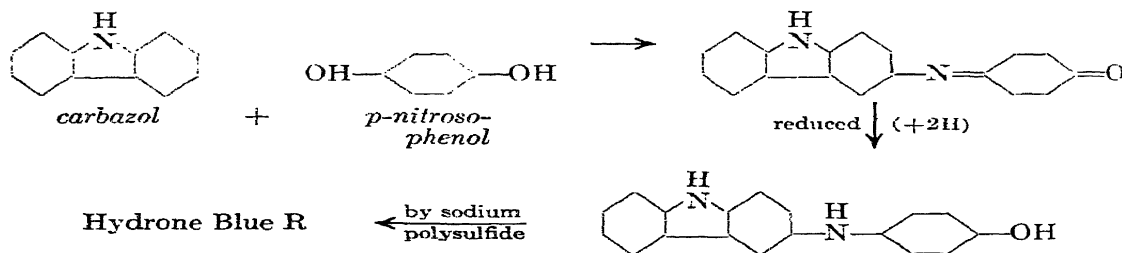
Hydrone Blue G is made from ethyl carbazol ($-N-C_2H_5$ instead of $N-H$) by condensing it with p-nitrosophenol; it gives a greener blue than Hydrone Blue R. Like the other vat dyes, Hydrone dyes must be reduced (sodium hyposulfite $Na_2S_2O_4$) in order to apply them to the fiber.

SULFUR DYES

The sulfur dyes are insoluble in water; they are reduced by sodium sulfide and thereby become soluble, so that they can be applied to the fiber; they are reoxidized to the insoluble compound on exposure to the air. The constitution is essentially unknown, but the proper raw materials and the conditions for obtaining definite colors are fairly well settled.

Meta-diamines, for instance meta-phenylenediamine, fused with sodium polysulfide, causes the evolution of hydrogen sulfide and a melt which yields brown and yellow dyes. Redder shades are obtained by using derivatives of azine; thus the methyl-aminooxyazine shown below,
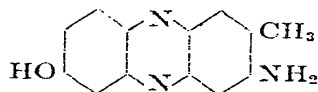
fused with polysulfide in presence of a copper salt, gives a Bordeaux color.

Blue shades are obtained by treating diphenylamine derivatives in alcohol solution with sodium polysulfide, which will be only partly dissolved: a water solution may be used also.

From
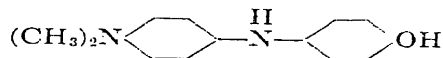
there is obtained Immedial Sky Blue. By condensing nitrosophenol and ortho-toluidine in 80 per cent sulfuric acid there is formed the body
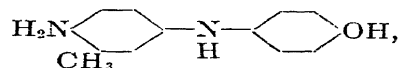
which treated with polysulfide in alcohol gives Thionone Blue. Similarly the condensation product of nitrosophenol and diphenylamine, with the formula

yields Pyrogene Indigo.

On refluxing in water or by heating under pressure meta-dinitrophenol with polysulfide there is formed Sulfur Black.

In order to isolate the dye, the procedure is to dissolve the melt in water and blow in air till all the dye has separated; it is filtered, washed, and dried in vacuum driers.

DYES FOR SYNTHETIC RESIN PRODUCTS

A spirit-soluble dye is made by adding to a water solution of a dye an acidified solution of diphenyl guanidine.[19] The dye treated may be directly soluble in water, or may require acidification for solution. The dyes which are suitable for this transformation must be found by trial; they belong to a number of classes. In order to bring about the reaction, the bath may have to be heated to boiling, or it may not require any heating. A precipitate is formed which is usually tarry. The clear liquid is decanted, and the tar dried, preferably under reduced pressure. Extensive use is made of these spirit soluble dyes for coloring synthetic molding resins, for which they are well adapted, as they dissolve readily in them.

Just which dyes will be suitable for the diphenyl guanidine treatment cannot be told before a trial; the only general statement which can be made is that any dyestuff containing an acid group in its molecule, so that its sodium salt will be water-soluble, is worth a trial (acid colors, direct colors, chrome colors, and certain eosine dyes).

Permitted Coal-Tar Food Dyes. The dyes listed herewith may be used for the artificial coloring of foodstuffs and beverages, provided they contain a minimum of 82 per cent of the pure coal-tar dye, and only a certain amount of specified impurities and moisture make up the remaining 18 per cent. The tests which must be used to establish the presence, absence, or quantity of the impurities are those which are published in the official bulletin.[20]

Ponceau 3R $C_{19}H_{16}N_2S_2Na_2$, a mono-azo dye, made by diazotizing crude q-cumidine and coupling with R acid; a dark red powder, giving a cherry water solution.

Ponceau S X $C_{18}H_{14}N_2O_7S_2Na_2$, a mono-azo dye, formed by coupling diazotized 1-amino-2,4-di-methylbenzene-5-sulfonic acid with 1-naphthol-4-sulfonic acid. It is a red powder, which dissolved in water gives red.

Amaranth $C_{20}H_{11}N_2O_{10}S_3Na_3$, a mono-azo dye, made by diazotizing naphthionic acid and coupling with R acid; a reddish-brown powder, giving a magenta-red water solution.

Erythrosine $C_{20}H_8O_5I_4Na_2$, the sodium salt of tetraiodofluorescein, a brown powder, which in water gives a cherry-red solution without fluorescence.

Orange I $C_{16}H_{11}N_2O_4S \cdot Na$, a mono-azo dye, made by coupling diazotized sulfanilic acid with α-naphthol; a reddish-brown powder, dissolving in water to give an orange-red solution.

Sunset Yellow F C F $C_{16}H_{10}N_2O_7S_2Na_2$ is a mono-azo dye, formed by coupling diazotized sulfanilic acid with β-naphthol-6-monosulfonic acid; the powdered dye is orange-red, and dissolves in water to give an orange-yellow color.

Naphthol yellow S $C_{10}H_4N_2O_8S \cdot Na_2$, a nitro dye, is the sodium salt of 2,4-dinitro-α-naphthol-7-sulfonic acid; a light yellow powder which in water forms a yellow solution, unaltered by either acid or alkali.

Tartrazine* $C_{16}H_9N_4O_9S_2Na_3$, a pyrazolone dye; it is a yellow-orange powder, soluble in water.

Yellow A B $C_{16}H_{13}N_3$, an oil-soluble mono-azo dye, is made by coupling diazotized aniline with β-naphthylamine; insoluble in water.

Yellow O B $C_{17}H_{15}N_3$, an oil-soluble mono-azo dye, is made by coupling diazotized ortho-toluidine with β-naphthylamine; it is insoluble in water.

[19] U. S. Pat. 1,674,128.

[20] Bulletin 1390 and supplement No. 1, "Chemistry and analysis of the permitted coal-tar food dyes," by Joseph A. Ambler, W. F. Clarke, O. L. Evenson, and H. Wales, Color Laboratory, Bureau of Chemistry, U. S. Dept. Agriculture, 1927-1930.

* Formula will be found elsewhere in this chapter.

Guinea Green B $C_{37}H_{35}N_2O_6S_2Na$, a triphenylmethane dye, is made by condensing benzylethylaniline-sulfonic acid with benzaldehyde, oxidizing, and converting the resulting product to the mono-sodium salt. It is a dull dark-green powder, dissolving in water to give a green solution.

Light Green S F Yellowish $C_{37}H_{34}N_2O_9S_3Na_2$, a triphenylmethane dye, has the composition of Guinea Green B with an additional sulfonic acid group; it is a reddish-brown powder which in water forms a green solution.

Fast Green F C F* $C_{37}H_{34}N_2O_{10}S_3Na_2$ is a triphenylmethane dye which is formed by condensing benzylethylaniline-sulfonic acid with para-hydroxy-ortho-sulfobenzaldehyde and oxidizing the resulting product. It is a reddish or brownish-violet powder, which when dissolved in water gives a bluish-green solution.

Brilliant Blue F C F $C_{37}H_{34}O_9S_3N_2Na_2$, the disodium salt of the triphenylmethane dye formed by condensing benzaldehyde-ortho-sulfonic acid with ethylbenzylaniline-sulfonic acid; it is a dark purple bronzy powder which dissolves in water to form a greenish-blue solution.

Indigotine $C_{16}H_8N_2O_8S_2Na_2$ is the sodium salt of the disulfonic acid of indigo,* preferably made from synthetic indigo; it is a blue-brown or red-brown powder, which dissolves in water to form a blue solution.

These dyes are listed in the order of their absorption of light in the visible spectrum, beginning with the red end, and proceeding toward the blue.

New Developments in Dyes. New developments in dyestuffs within the last few years, which are of major importance both as to value and quantity produced are (1) the Neolan Dyes, (2) Celanese dyes, (3) Polar or Milling Dyes, (4) Hansa Yellows, (5) the Naphthols, (6) Stable Diazo Salts, and (7) Rapidogen Dyes.

(1) The Neolan Dyes (Soc. Chem. Ind. in Basel) or Pilatus Dyes (I. G.) are acid azo dyes containing a co-ordinated metal atom in the dye molecule.[21] It is a well known fact that "Chroming" dyes after they have been applied to the fibre by the addition of chromium salts to the exhausting dyebath increases their stability or fastness to light and washing.

These new dyes are azo dyes made in the usual manner, except that before isolation the solution of the dye is treated with a chromium salt, such as chromium formate under reflux or pressure, and the dye is then isolated. As a result, the chromium salt of the dye is formed before application to the fibre eliminating the necessity of a two step operation during the dyeing. The fastness to light and washing is as good as can be obtained with the older method of dyeing.

Approximately 150,000 lbs. of these dyes were imported into the United States during 1935.

(2) Fabric made from cellulose acetate (Celanese), can not, as a rule, be dyed with the ordinary cotton or wool dyes. In recent years, with the increase in popular use of Celanese goods, a new group of dyes have been developed particularly for this textile alone.

The production of these, the Celliton (Gen.), Setacyl (Geigy), Celanthrene (Dupont), Nacelan (National) dyes with various other brands totaled almost 2½-million pounds in 1935. They are made by dispersing water-insoluble organic compounds, usually basic in nature, by means

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* Formula will be found elsewhere in this chapter.
[21] British Patent 210,890 (1929); German Patents 369,584; 369,585; 433,148; U. S. Patents 1,693,448; 1,796,058; 1,844,396; 1,844,397; 1,844,398; 1,887,602; 1,893,557.

of soaps or sulfonated fatty alcohols, into the colloidal state.[22] As colloidal particles these dyes can be applied to the cellulose acetate.

1-4 Diamino Anthraquinone

violet
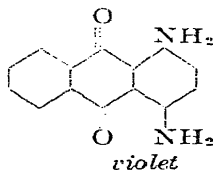
and Amino Azo Benzene

yellow
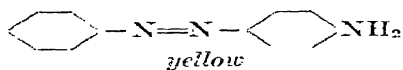
are typical compounds used in these dyes.

(3) Polar or Milling colors are used on woolen fabrics, such as bathing suits or rugs which are subjected to sunlight and wear. They are dis-azo dyes, the third component being a phenol, which is further condensed with para toluol sulfonyl chloride, markedly increasing the fastness to acids and sea water.[23]

(4) Perhaps the most outstanding advance in the pigment field has been the introduction of the Hansa Yellows.[24] These colors are clear, bright, light fast yellows, in many respects better than the inorganic chrome yellows when used for the present day lacquers or paints. They are azo dyes made by diazotizing amines, or nitro or chlornitroamines and coupling the diazonium compounds to acetoacetanilide or its derivatives.

Hansa Yellow
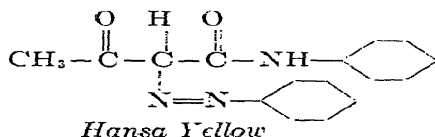
(5) The "Naphthols" are second components for developed dyes, similar in method of application to Beta Naphthol, but giving more variations in shade and better light and washing fastness. The Naphthols are arylides of Beta Oxy Naphthoic acid.[25]

For example, Naphthol AS is
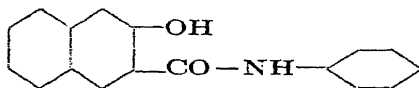
[22] U. S. Patents 1,448,432; 1,610,916; 1,618,413; 1,618,414.
[23] U. S. Patents 1,067,881; 1,602,776; 1,893,244; British Patent 26,908 (1913).
[24] U. S. Patents 1,059,599; 1,051,565; 1,644,003; 1,082,719.
[25] U. S. Patents 1,101,111; 1,935,554; 1,819,127; 1,971,409; 1,457,114.
J. Soc. Dyers and Colourists, **40,** 218 (1924); **96,** 229 (1930).

Amines, other than aniline, can be condensed with the COOH group of the Beta Oxy Naphtholic Acid in the presence of a dehydrating agent as PCl_5, etc., forming other members of this popular series of dye intermediates. In physical appearance they are usually light tan.

They are dissolved in an alkaline solution and are applied or "padded" on the fiber which in then run through a solution of a diazo. Coupling takes place in the α position.

Using various numbers of the Fast Salts (Stable diazo salts), shades on cotton from yellow to black are available. Colors made from the Naphthols are usually insoluble in water and hence are used for pigments and textile printing.

Production and imports of the Naphthols for 1935 totaled more than 6,000,000 lbs.

(6) With the Naphthols came the development of the stabilized diazonium salts, the Fast Salts (Gen.),[26] solutions of which can be used in place of preparing the diazo solution from the amine in the dyehouse. Their manufacture is described in an earlier paragraph.

Imports alone for these Fast Salts for 1935 amounted to 445,695 lbs.

(7) The use of the Naphthols and Fast Salts led further to the development of the Rapidogens and Rapid Fast Colors.

The Rapidogens [27] are mixtures of diazamino derivatives of amines, for example,

$$\langle \rangle - N = N - N \Big\langle \begin{array}{l} CH_3 \\ CH_2COOH \end{array}$$
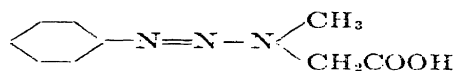
with Naphthols in molecular proportions. As such they have no color. However, when made into textile printing pastes with suitable thickening agents and applied to the cloth from printing rolls, the color is formed by subsequent treatment in slightly acid vapors, (acetic acid) in a steam chamber.

The Rapid Fast Colors are the nitrosamines of the diazo bodies, likewise mixed with molecular proportions of the Naphthols. They, too, are applied to the fabric by printing and the color is developed in the acid ager.

The principle underlying these types of dyes is that the diazamino or nitroso group can readily be converted to the diazo by the action of the acid vapors. Then before the diazo has had time to decompose it couples with the Naphthol which was present in the mixture as purchased.

These dyes compete with the vat dyes because of ease of application which offsets the greater light fastness of the vat dyes.

Uses and Production. Dyes go to the textile industry, paper industry, leather, foodstuff, fur, pigment, synthetic resins, boot polish, printing ink, and many other industries. A color confined to one industry, for example, the woolen industry, would be standardized on wool; on the other hand, Nigrosine, Citronine, Resorcine Brown are tested on vegetable-tanned leather.

[26] U. S. Patents 1,572,715; 1,975,409; German Patent 94,495.
[27] U. S. Patents 1,882,560; 1,882,561; 1,882,562; 1,858,623; 1,505,568; 1,505,569.

All dyes and dyestuffs, when isolated, have to be dried, milled and standardized. Drying is done in vacuum shelf driers, hot air chambers. Milling is done in a disintegrator, or ball mill. The diluents added are salt, anhydrous sodium sulfate, dextrin, and others.

For dyes which have a minimum of salt, pressing in the hydraulic press, for the removal of the greater part of the adhering water, is coming into general use.

Of interest is also the fact that, at times, a second dye is a by-product, and must find an outlet; thus when one ton of Oxyphenine Yellow 2G is made, one ton of Primuline is simultaneously produced.

The production in the United States for the year 1935 is indicated by a few selected figures (from Census of Dyes, 1935, U. S. Tariff Commission).

U. S. 1935 Dye Production.

	Pounds	Value per Pound
Acid dyes	14,269,831	
Direct dyes	26,073,439	
Sulfur dyes	16,949,143	
Vat dyes	27,908,296	
Food dyes	323,918	
Total	101,608,743	53 cents

For comparison, and because the dyes are itemized somewhat differently, the figures for 1930 are given below:

U. S. 1930 Dye Production.

	Pounds	Unit value per pound Cents
Mono-azo	7,209,622	48.7
Dis-azo	10,109,814	51.4
Tris-azo	8,183,730	31.6
Total azo	28,740,179	49.6
Triphenylmethane	2,518,282	107.6
Azine	2,483,507	42.8
Sulfide	14,232,076	17.0
Anthraquinone vat	4,197,338	129.4
Food dyes	304,912	255.0
8 other classes, including indigos	24,819,359	28.9
Total, all dyes	86,480,000	42.9

In contrast to the considerable production, the imports of dyestuffs in 1935 were 3,638,199 pounds of dyes; in 1914, the imports were over 45 million pounds.

OTHER PATENTS

German Patent 145,373, on phenylglycine production; U. S. Patent 1,431,306, on brilliant indigo; German Patent 237,262, U. S. Patent 1,012,363 and 1,473,887, all on indigo derivatives; 1,877,800, manufacture of tri-azo dyes, and 1,821,290, of di-azo dyes; 1,848,228, method for making black and gray vat dyes, comprising the condensation of a sulfonated benzanthrone compound with hydroxyl amine, followed by alkaline fusion; 1,759,264, manufacture of new sulfur dyes; 2,029,313, production and application of new dyestuffs for cellulose ester and ether by means of an unsulfonated anthraquinone compound; 2,069,158, dis-azo dyestuffs, insoluble in water, a developed dye for cotton.

PROBLEMS

1. Azo dyes are manufactured from a bill of materials which lists the pounds of the various ingredients, their percentage purity, the molecular weight, the mols used, and the molecular equivalents represented. The molecular weight is the theoretical one, but the mols used and therefore the mol equivalent includes the excess necessary to drive the reaction to an end, or to exhaust any certain ingredient. Such a list includes items for caustic, soda ash, acids, sodium nitrite and other inorganic chemicals. Working in a simpler way; set up the bill of materials which are required to make 924 pounds of Direct Blue 2B, assuming that the yields are perfect, and that theoretical quantities will lead to a complete reaction.

Start with the proper weight of benzidine; make it into diazotized benzidine, then follow the description in text.

2. The yield of indigo powder based on the phenyl glycine, let us assume to be 75 per cent. How much indigo blue and from it, indigo white will be obtained from 600 pounds of glycine? How much sodamide will be required, and how much indoxyl is formed? The hydroxides used are twice the weight of the potassium glycine; what size pot will be large enough to allow the fusion? The general shape should be as indicated by the fusion kettle in Chapter 27.

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About 100 years ago the French chemist, Chevreul, demonstrated that oils and fats such as olive oil and lard were glycerides of fatty acids; on this knowledge as a basis the handling and refining of edible oils and fats was remodeled. Some twenty years ago two French scientists. Sabatier and Senderens, made another important contribution to this field when they transformed oleic acid, an oil, into the solid stearic acid; based on this reaction, technologists from every land have constructed a number of devices, so that to-day the "hardening" of edible oils into edible fats is a well-established branch of this industry.

Chapter 29
Animal and Vegetable Oils, Fats, and Waxes

The animal and vegetable oils, fats, and waxes are esters of organic acids belonging to the fatty acid [1] series. An ester is formed by the combination of an alcohl and an acid, with the elimination of water. The animal and vegetable oils and fats are glycerin (really, glycerol) esters of a wide variety of fatty acids, in which the glycerin is the alcohol; while the waxes are esters of the same kind of acids, but the alcohol is some other one instead of glycerin. The fatty acids belong chiefly to three or four subdivisions; to the saturated series (stearic acid), to the oleic series (which is unsaturated, lacking two hydrogen atoms), or to more unsaturated series lacking four and more hydrogen atoms.

The glycerides of the saturated series melt higher than those of the oleic series. A fat is rich in glycero-stearate, and has some glycero-oleate admixed; while an oil would be rich in glycero-oleate and poor in glycero-stearate. But among the glycerides of the saturated acids, a further consideration must be made. One molecule of glycerin requires three molecules of acid to form an ester. If the three acid residues are the same, the fat is rather hard, thus glycero-tristearate, called stearin for short, melts at 72° C.; if the three acid residues are unlike, the fat has a lower melting point, thus glycero-distearate-monopalmitate, which melts at 63° C.

$$
\begin{array}{l}
CH_2\text{—}OH \\
CH\text{—}OH + 3C_{17}H_{35}COOH = \\
CH_2\text{—}OH
\end{array}
\qquad
\begin{array}{l}
CH_2\text{—}O\text{—}OC.H_{35}C_{17} \\
CH\text{—}O\text{—}OC.H_{35}C_{17} + 3H_2O \\
CH_2\text{—}O\text{—}OC.H_{35}C_{17}
\end{array}
$$

glycerin   *stearic acid*   *glycero-tristearate* (an ester)
(an alcohol)
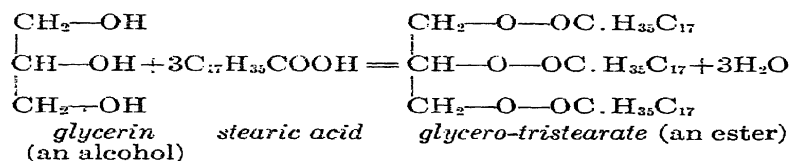
In each oil and fat, a number of different fatty acids occur, sometimes as many as ten, while six or more is the rule; this would make the study of the composition of an oil difficult enough. The complication of mixed esters such as glycero-distearate-monopalmitate raises the difficulty still

[1] It is because of their presence in fats that these acids have been named fatty acids.

further; it is therefore not surprising that there are many oils and fats whose composition is still unsettled.

The study of the composition of the oils and fats is based on a knowledge of the constituent fatty acids, a number of which are listed in Table 60, with the names of oils and fats in which they occur; these latter are merely examples, for each fatty acid occurs in a large number of oils and fats.[2]

TABLE 60.—*Fatty Acids Occurring in the Form of Esters in Oils, Fats, and Waxes.*[*]

| | | Group A—Saturated series | | |
		Melting point of the free acid	Melting point of the simple triglyceride	Chief occurrence
Butyric	$C_4H_8O_2$	liquid	liquid	butter fat 4%
Capric	$C_{10}H_{20}O_2$	31.3° C.	liquid	butter fat, coconut oil
Laurie	$C_{12}H_{24}O_2$	43.6	45	coconut oil 45%
Myristic	$C_{14}H_{28}O_2$	53.8	56.5	butter fat 22%
Palmitic	$C_{16}H_{32}O_2$	62.6	65	palm oil, lard
Stearic	$C_{18}H_{36}O_2$	69.3	72	all fats
Carnaubic	$C_{24}H_{48}O_2$	74	—	carnauba wax
Cerotic	$C_{26}H_{52}O_2$	78	76.5	beeswax
Mellissic	$C_{30}H_{60}O_2$	90	89	beeswax
		Group B—unsaturated, lacking two hydrogen atoms		
Oleic	$C_{18}H_{34}O_2$	14	liquid	olive oil 70%
Erucic	$C_{22}H_{42}O_2$	33	31	rape oil; fish oil
		Group C—unsaturated, lacking four hydrogen atoms		
Linolic	$C_{18}H_{32}O_2$	—	—	cottonseed oil and soya bean oil
		Group D—unsaturated, lacking six hydrogen atoms		
Linolenic	$C_{18}H_{30}O_2$	—	—	linseed oil 10%
Isolinolenic	$C_{18}H_{30}O_2$	—	—	linseed oil 60%

Note: "Coconut 45%" means that of the fatty acids present in coconut oil, 45% are lauric acid.
* Mainly from J. Lewkowitsch, "Chemical technology and analysis of oils, fats, and waxes," 3 vols. New York and London, Macmillan Co.

The most important vegetable oils are cottonseed, linseed, olive, corn, peanut, rape, coconut, palm, and castor. The method of extraction is similar for all. The fruit or seed after cleaning by sieving and blowing, or by hand selection, is crushed and first cold-pressed for the highest grade, then pressed warm for technical grades; the crushed mass may be extracted still further by solvents. In the case of edible oils, the first grade is used for food purposes; the lower grades are used for technical purposes, including the making of soap. In order to be edible an oil must be attractive; it must possess an agreeable flavor (olive oil) and must be free from disagreeable odor. It must be pale in color, usually yellow; it may be without attractive odor, yet be wholesome and well suited for food. The oils used as salad oils in the United States are olive oil, mainly imported, corn oil, peanut oil, and cottonseed oil (Wesson oil is cottonseed oil). The chief use of linseed oil is in varnishes and paints; of rape oil for lubricants, coconut and palm oils mainly for soap

[2] Except butyric acid which is characteristic for butter fat.

making. Vegetable fats are mainly artificial, made from the oils, such as cottonseed oil, by hydrogenation.

Animal oils and fats are: whale oil, fish oil (both less important now than formerly); by hydrogenating them, fats are formed, which are used in part for soap stock; lard and lard oil, for food; beef, mutton, and sheep tallow; cod-liver oil for pharmaceutical purposes; sperm oil, a liquid wax, for lubrication. The method of extraction is essentially a warming so that the oil may run off or be pressed out. The best-known waxes are carnauba wax and beeswax.

It will be noted that nothing has been said about distilling; none of the oils and fats can be distilled under atmospheric pressure without decomposing at least partly. They are called fixed oils, in distinction from the odoriferous oils in the following chapter under the general name of essential oils, which are frequently distilled. The oils obtained from petroleum may also be distilled, but they remain well characterized as one group because of their mineral origin. In discussing paints and varnishes, the point of view of the varnish maker is adopted, who thinks of oils as drying, semi-drying, or non-drying oils. It is the state of unsaturation indicated for certain fatty acids in the table (groups C and D), which permits the so-called drying because of oxidation by the air[3]; it is the same unsaturation which is relieved in another fashion by hydrogenation.

In order to compare successive shipments of the same oil, and in order to detect adulteration, a number of tests are applied, some of which are very old. In the Maumené test, the heat caused by the addition of sulfuric acid is measured. The saponification test records how much potassium hydroxide is consumed in forming the potassium salt of the fatty acid; an admixed mineral oil would not consume any caustic and would thereby be detected. The iodine value gives a measure of the unsaturation. Specific gravity and the refractive index in conjunction with the tests named above, and at times confirmable by specific tests, permit identification of the oil and estimation of its purity.[4]

The color of oils is lightened by adding fuller's earth, bone char, precipitated silica or similar finely divided substances, followed by a filtration.

The extraction of linseed oil will be described in detail; the procedure for other seed-oils is similar.

LINSEED OIL

Linseed oil is made by pressing warmed flaxseed[5] which has been previously crushed. Flax is grown in several northwestern States, notably in North Dakota, Montana, Minnesota, and South Dakota. The bulk, however, is imported from Argentina, so that linseed oil refineries are

[3] *Compare* under varnishes in Chapter 31.

[4] "Standard methods of chemical analysis," W. W. Scott, New York, D. Van Nostrand Co. "Chemical technology and analysis of oils, fats, and waxes," J. Lewkowitsch, London and New York, Macmillan Co. "Vegetable Fats and Oils," G. S. Jamieson, New York, Chemical Catalog Co., Inc., 1932.

[5] Formerly called linen seed.

located at ocean ports as well as at inland points. The main product is the oil, but an important by-product is the press cake, which forms a valued cattle food.

The flaxseed is stored in elevators very much as grain is. For the expression of the oil, the seed is elevated to the top of a five-story building so that in subsequent operations it may be fed by gravity. First it passes horizontal screens which remove all coarse admixed matter; then it is fed to a rotary bag blower with numerous small conical bags. These are connected periodically and automatically with compressed air, which blows out the chaff and small dirt. The clean seed is carried by a screw conveyor to one of a number of large storage bins; the crushing rolls are situated under them on the next floor. It may be interesting to note that flaxseed is slippery; stepping into a tall bin means that a man will go to the bottom. The seed is small, about 3 mm. long, 2 mm. wide, and 1 mm. thick, so that it will escape through the bottom of a farm wagon unless the boards are brought close together.

The crushing device consists of 5 heavy steel rolls placed in a vertical line; the two upper rolls are corrugated. Three rolls are driven, the first, third, and fifth; the second and fourth are idle. The speed is 175 rpm. The seed from the bin is fed by gravity to the top roll; by means of small troughs, the meal is collected from one roll and fed to the next, making four passages in all. A completely mashed product results, which has lost all trace of shape. The mashed meal passes by gravity to a two-stage steam-jacketed kettle provided with slow agitation (30 rpm.). The meal enters the kettle in the center of the first shelf, and passes to the second shelf through circumferential openings. It is drawn from here as required.

The actual pressing is controlled by two men, who operate a battery of six presses, three on a side; each press has thirty horizontal shelves. In order to form the meal into a slab-like section, a frame 18 inches wide and 3 feet long is placed on a hair mat of slightly larger size and pushed under a slide in the bottom of the kettle, whose base is just above the working table. The frame is filled by opening the slide; the mat and frame are pulled out and lightly pressed into shape by an automatic ram. The frame is removed and another similar mat placed over the meal. Three such mats are made ready each minute.

One of the six presses is always open, in process of being unpacked and at the same time reloaded; the pressed cake from the previous pressing is removed and in its place a fresh charge slipped in. Below each sixth shelf a wider metal tray is inserted to collect the oil and guide it through funnels and pipes to the main trough in the floor. It takes 10 minutes to empty and fill a section; the cycle for the press is 60 minutes, with 50 minutes actual pressing. The mats lie in horizontal planes; the pressure is applied by a hydraulic ram which rises in the vertical plane, from below. The pressure applied is 4000 pounds, and is transmitted by means of linseed oil, constantly changed to prevent its turning rancid. Linseed oil is used so that contamination by some foreign oil may be

avoided. Each section presses 5½ bushels[6] of seed per hour (hence also per cycle), or 132 bushels per day, yielding 6.8 barrels[7] of oil. For the battery of six presses, the production is 40 or 41 barrels. It may be estimated that 20 bushels of seed are required to produce 1 barrel of oil. The number of batteries in a plant varies, but is usually very high. The oil obtained is about 34 per cent of the weight of the seed.

The pressed cake, which resembles a stiff board, is laid on small trucks or on a conveyor which brings it to the trimming machine. The edges are cut off because they still contain 30 per cent of oil; these trimmings are returned to the warming kettle. The body of the cake retains 5 to 6 per cent of oil, which is not removed. It is broken into small pieces by a rotating cylinder with projections, and made into a powder in squirrel-cage disintegrators[8] with 52-inch baskets, rotating at extremely high speed. The press-cake powder is shipped in 100-pound bags. So important has this by-product become that the fluctuations in its price[9] are reflected in the price of linseed oil.

There is also in use a continuous process of extraction, in which the warm meal is pressed by a tapering screw; the pressed cake retains about 10 per cent of oil.

In 1935, the production of linseed oil (U.S.) was 483,025,310 pounds, valued at 9 cents a pound, and that of the cake and meal 470,760 tons, valued at $28.50 the ton ($48.30 in 1929).

Refining the Oil. The oil from the press, filtered through duck and flannel filter cloths in a plate-and-frame press, is the raw linseed oil of commerce; its color is a yellow-brown.

Large quantities are refined further by gentle heating for definite periods to remove moisture, and by adding fuller's earth followed by filtering through duck, flannel, and thick paper. The heating must be carefully regulated in order to avoid darkening the oil. The effect of the fuller's earth addition is partly to bleach the oil, partly to assist in the removal of finely suspended matter, called the "foots." For many purposes the oil must be "blown" in order to give it body, that is in order to raise the viscosity. This may be done by heating with steam coils and blowing in air for certain periods. The blowing is usually followed by a filtration.

Although linseed oil will "dry," that is, harden on exposure to air, through oxidation, such drying is too slow for practical purposes. The drying is greatly accelerated by adding small amounts of the oxides of lead, manganese or cobalt,[10] and then heating the oil under reduced pressure; the product is "boiled linseed oil," which dries in a few hours. The metals act as catalyzers in the oxidation.

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[6] A bushel of flaxseed weighs 56 pounds.

[7] A barrel contains 50 U. S. gallons.

[8] Chapter 44.

[9] The press-cake meal sells normally for $40 to $45 a ton.

[10] Three-tenths per cent lead oxide, 0.1 per cent manganese dioxide, or 0.05 per cent cobalt oxide have the same accelerating power; a mixture of any two is still better. Iron oxide is also effective but it is not favored because it discolors the oil.

When fresh, linseed oil is edible. For that purpose it is expressed cold; this is done on the continent of Europe to some extent.

The special tests for various grades of linseed reflect its chief use, that of a drying oil in paints and varnishes. In addition to the usual tests, its color, drying power and sediment content (the foots) are observed.

<div align="center">VEGETABLE OILS</div>

Olive Oil. Because of its flavor, olive oil is the most highly prized of the edible oils. The olive tree is cultivated in Italy, southern France (Provence), Spain, Algeria, Tunis, and southern California. In general, the fruit is picked just before it is ripe; its content of oil varies from 35 to 60 per cent. The pressing for the highest grade is done cold, sometimes with the stone, other times after the stone has been removed. The fruit is packed in muslin bags and placed in a cylindrical cage surrounded by a sheet-steel envelope to catch the squirting oil. A heavy cylinder is applied from above, with gradually increasing force by means of a hand-operated screw. The oil collects in the floor trough. The color is pale yellow.

The pulp is mixed with cold water and pressed again, best with hydraulic pressure, and a second quality of edible oil is obtained. Made up with hot water, still another quality of edible oil is secured. Finally the pulp is extracted with carbon disulfide, which gives a dark product suitable for soap making. There is a difference in composition in the various grades. The free fatty acids, resulting from hydrolysis, are less than 1 per cent in the highest grade, 5 per cent in the next grade, and as high as 20 per cent in the technical grade.

Olive oil contains mainly the glyceride of oleic acid, an unsaturated acid; it is a non-drying oil.

Peanut Oil. This oil is a very acceptable substitute for olive oil. It is obtained by pressing the peanut, or earth-nut, and is called in Europe arachis oil from the name of the plant, *Arachis hypogœa*. The seeds or nuts contain 43 to 46 per cent of oil. The shells and skins are removed, the nuts are ground in squirrel-cage disintegrators, and cold-pressed first, when 18 per cent of the oil is obtained. This grade is used for salad oil, and has a pleasant nutty flavor. Two more expressions at higher temperature furnish technical grades.

Corn Oil. When starch is made from corn (maize) there is obtained as a by-product the kernel, which on pressing in the same way as flax-seed is pressed, yields an oil, and a press cake which is a cattle food. The corn seed contains 50 per cent of oil; pressed cold a pale yellow product is obtained with a slight odor. This is removed by refining and the oil finds a market as a salad oil, in part under the name of Mazola oil in the United States. The lower grades are used for soap making, to a limited extent in paints and varnishes.

Palm Oil. The best grades of palm oil are edible. The fresh fruit is pressed slightly warm, and a pale yellow, butter-like material obtained;

its consumption is limited to the natives of West Africa,[11] where the palm *Elæis guineensis* grows. The greater part of the oil is obtained by allowing the fruit to ferment in holes in the ground, then either pressing the softened fruit, or boiling it in water and collecting the oil which rises. The oil so obtained is suitable only for technical purposes, largely soap making. Several other varieties of palms are cultivated in South America, and worked for oil.

The palm kernels are collected separately and yield a soft fat of different composition from palm oil. The kernels are generally imported to Europe and the United States and utilized with modern working methods.

Cottonseed Oil. The oil produced in the greatest quantity in the United States is cottonseed oil. Its production is twice as great as the production of linseed, which in turn is five times the combined imported and home-produced olive oil. Table 61 below indicates the relative importance of a number of the important oils.

TABLE 61.—*Production and Imports of Vegetable Oils in the United States for 1935 Based on Figures from the Bureau of the Census, Department of Commerce. The Figures Are in Pounds, and for the Crude Oil, Unless Otherwise Designated.*

	Production	Imports	Exports	Consumption
Cotton-seed oil	1,184,038,860	28,597,488	3,655,133[r]	1,182,334,379
Lin-seed oil	502,043,424	2,232,451	986,109	291,683,903
Coconut oil	252,841,492	363,396,002	12,259,233	542,041,069
Olive oil edible	664,225	70,788,530		2,431,757
Palm oil	none	297,579,208	small	251,292,538
Palm kernel oil	none	50,592,641*	12,063,140	58,909,726
Corn oil	99,787,789	25,746,090	833,101	135,761,118
Castor oil	46,627,313	small	small	25,762,198
Peanut oil	44,673,069	80,723,225	712,385	101,122,181
Soybean oil	105,056,204	14,248,574	4,111,188	100,882,342
Rapeseed oil (colza)	none	60,297,893	small	35,801,697
Tung oil	none	120,058,817	4,924,004	114,286,682
Sesame oil	64,977,447	small	small	54,251,526

*In addition to this amount of crude, 7,977,812 pounds of edible palm kernel oil were imported.

r = refined.

The cottonseed contains 20 per cent of oil; each pound of cotton brings two pounds of seeds. The shell is cut by rotary knives and separated from the seed proper in a wire gauze basket which rotates, letting the seeds pass and retaining the hulls. The decorticated seeds are crushed and pressed; crude cottonseed oil red or brown in color is obtained. It is refined by warming it with a solution of caustic soda which removes much of the color and neutralizes the free fatty acids. The caustic solution forming the lower layer is run off, and the remaining oil washed. On standing in the cold, solid glycerides separate, and are removed by filtering under pressure. The oil may be bleached further by adding fuller's earth, and filtering; edible grades are prepared in this way. It is used to some extent as an oil, to a constantly greater extent for hydrogenation, which gives cooking fats. It finds considerable use in making butter sub-

[11] Except for a small quantity placed in some margarines for color.

stitutes. Formerly it was largely used for making hard soap; to some extent soya bean oil has displaced it. Cottonseed oil is a semi-drying oil.

There were produced in 1935 1,108,582,294 pounds of cottonseed oil, valued at 8.26 cents a pound; in 1933, the price had been 3.23 cents per pound. The cake and meal produced in 1935 were 1,614,345 tons at $33.50 a ton ($14.04 in 1933). Linters were 805,083 bales at $26.90 a bale ($8 in 1933).

Coconut Oil. The cocoa palm grows in South America, India, Cochin-China, in the Philippine Islands, and other countries. The fruit is imported in the dried condition under the name of copra. The oil is expressed at 60° C., and is edible, either as such or mixed in margarines. The press cake is a cattle food.

The production of coconut oil is next to that of linseed oil (for the United States).

Soya Bean Oil. The soya bean contains 20 per cent of oil; it is grown chiefly in Manchuria, where the oil is also extracted. The method is to steam the bean and to press it warm; the yield is about 10 per cent. Soya bean oil is a semi-drying oil, and is used in varnish making, also for soap. The soya bean has been raised for forage in the United States, but not in any great quantity for oil production as yet.

Castor Oil. Castor oil is obtained from the seed of the castor plant *Ricinus communis*, which grows in the West Indies, India, and other tropical countries. The seed contains 45 to 50 per cent of oil. The best grade, the cold-pressed oil, is widely used as a mild cathartic. Other grades are valuable as lubricants, mixed with mineral lubricating oil. Castor oil is a non-drying oil; it is a plasticizer for Celluloid and for lacquers.

Soluble Castor Oil or Turkey Red oil is sulfonated castor oil. Concentrated sulfuric acid is mixed with castor oil at temperatures not exceeding 35° C.; after some time, a small amount of water is added, and the dilute acid formed, which separates as a lower layer, run off. The oil is washed with a sodium sulfate solution. Ammonia is added in amount insufficient to neutralize the remaining acid, but sufficient so that the oil gives a clear solution with water. The soluble oil is used extensively in the preparation of the fibers for dyes (Chapter 26).

Rape Oil. The rape oil, *Brassica campestris*, is cultivated in Europe; seeds are also imported from India, and oil from Japan. The seed has 40 to 45 per cent of oil; the treatment is similar to that of flaxseed, and the presscake is a cattle food. Rape oil has non-gumming properties, and finds extensive use as a mixed lubricant, with mineral oil.

Sesame Oil. Sesame oil is of some importance in Europe. The sesamum seed is imported from China and India. The best grades are edible, either as salad oil or in margarine; the lower qualities serve for soap making.

Chinawood Oil, or Tung Oil. The seeds (*Aeurites cordata*) in a nut the size of a small orange contain 53 per cent of oil, the tung oil. Pressed by native methods, 40 per cent of the oil is expressed. In China,

this oil is used by the river men to impregnate the wood of boats and rafts in order to make them waterproof, hence the name, "China wood oil." This oil has gained a tremendous importance in varnish making; it dries in one-third the time which linseed oil requires, and has other valuable properties of its own. Chinawood oil consists chiefly of the glyceride of elacostearic acid. Within the past ten years trees have been planted in the United States, chiefly in Florida. An experimental farm has recently been established in Mississippi.

ANIMAL OILS AND FATS

Whale Oil. Whale oil formerly was an important source of oil for burning; the advent of petroleum products has relegated it to an unimportant position. The annual world's production of whale oil is about the amount of olive oil imported into the United States. The seats of the whaling industry are Norway, Iceland, and the American Pacific coast.[12]

A large whale yields between 100 and 180 barrels of oil; the blubber or fat is rendered either on board boat or in the home port. The fat is chopped fine and rendered by heating first by itself, then with water; certain parts of the carcass may also be digested for oil. The uses are: for leather dressing, burning oil, soap, and, mixed with mineral oil, for lubricant. Whale oil is also hydrogenated to a fat.

Fish Oil. Fish oil is obtained by boiling either the whole fish or selected parts in water and collecting the oil which rises. The menhaden, herring, and certain salmons are used in large numbers for this purpose, and many other fish in smaller numbers. The residue in the rendering pots is dried and sold for fertilizer. Fish oil is used in cheap paints to replace part of the linseed oil and for other minor purposes. The oil may be hydrogenated to a fat, at the same time losing its unpleasant odor; such fats are suitable for soap making (1935 production about 55 million pounds).

Cod-Liver Oil. The cods are brought to the home station alive, with steam trawlers, opened and the fresh livers heated in steam-jacketed kettles. The first oil is prized for its vitamin content, and is used for medicinal purposes. On continued heating a second grade of oil is obtained, which is used in fine poultry raising. Livers which are brought in partly decomposed are rendered for an oil used in the dressing of leather (1935 production 1.1 million pounds).

Lard and Lard Oil. The fat of the pig is rendered by heating it with water in closed cast-iron vessels under pressure and provided with an outlet for the release of overpressure caused by the formation of gases. After digesting, the liquid is run off; by cooling it moderately, a division

[12] There are 4 shore stations, each handling whales caught within a radius of 150 miles: Moss Landing, Trinidad, in California; Bay City, Washington; Akutan, Alaska. Production in 1930, 10 million pounds. The most important whaling grounds of the world to-day are in the Antarctics, particularly near Ross Sea. (From the Bureau of Fisheries, Department of Commerce, Washington, D. C., and Bureau of the Census.)

into the liquid part, the lard oil, and into a solid part, the lard proper, is made. The lard oil is called oleo, and is made into oleomargarine, a butter substitute (1935 production over 1.6 billion pounds).

The operation of rendering has recently been improved and accelerated. In the circulating rendering process of Wurster and Sanger, Chicago, several desirable ends have been reached: (1) Quick heating, which reduces the time factor and the objectionable yellow color; (2) low temperature, avoiding scorching; (3) larger capacity for a given time period.

FIGURE 170.—A circulating rendering plant. (Courtesy of Wurster and Sanger, Inc., Chicago.)
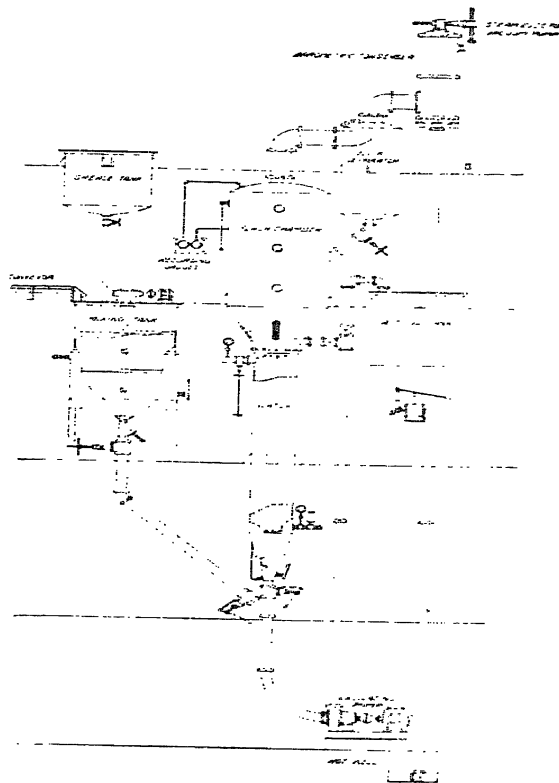
The equipment for this process includes a tubular heating element with vertical tubes through which the ground material passes, flash chamber, a circulating pump, separator, and a vacuum pump. The tubes are heated by exhaust steam, under 5 pounds pressure. The material is drawn from the base of the tubes by a centrifugal pump of the non-clogging type, and is returned at a point just above the tubes. The heater is surmounted by a flash chamber in which the gases evolved are collected before they pass to a separator where the droplets of entrained fat are recovered, to be returned to the main drum. From the separator, the

gases go to the steam ejector, which maintains a low pressure on the system.

After the material is completely melted, it is discharged into a settling tank, from which the clear fat is drawn off. The sediment, called cracklings, is run to the filter press.

With a heating surface of 1000 square feet, a charge of eight tons is rendered in two hours. Compared with the older type of jacketed melters using high pressure steam (50 pounds), it is found that the new rendering process equipment works four times as fast, besides producing a paler product.

Several other details are exhibited in Figure 170.

Tallow. By tallow is usually meant beef tallow, which is rendered in the same way as lard. There is also a mutton tallow, a sheep tallow, and others. Their chief use is for soap making [13] (1930 production ½ billion pounds).

Butter. The cream in cow's milk isolated in a centrifugal separator is rich in small globules of fat, which coalesce on churning; the lump so formed, after addition of salt (in the U. S.), is table butter; it is about 83 per cent butter fat, the rest water and salt.

WAXES

Sperm Oil. Sperm oil is obtained principally from the content of a cavity in the head of the cachalot or sperm-whale. When the oil is cooled it deposits a solid wax, the spermaceti, used in pharmacy and in candle making. The oil under the name of sperm oil is valued as a lubricant for light, high-speed machinery; like rape oil, it has no gumming tendency. The chief ester in spermaceti is cetyl palmitate, $C_{16}H_{33}O.OC.C_{15}H_{31}$. Cetyl alcohol is a monohydric alcohol $C_{16}H_{33}OH$. Sperm oil similarly contains alcohols combined with fatty acids different from glycerin (1935 production about 1 million pounds).

Carnauba Wax. Carnauba wax is found on the leaves of a palm tree in Brazil, the *copernicia cerifera*. The leaves are gathered and rubbed to dislodge the coating: it is purified by melting, decanting from the deposit, and cooling. It has a high melting point, 105° C., and is used in the varnish industry and in furniture and shoe polishes and in carbon paper coating.

Beeswax. Beeswax is obtained from the honeycomb of the common bee; it is purified by washing and bleaching. Industrially, it is of small importance.[14]

HYDROGENATION

The hydrogenation of oils with the aid of a catalyst is an established industry. The reaction is used mainly for the hardening of vegetable

[13] Lard m.p. 36° to 40° C.; tallow, 40° to 45° C.

[14] Some other vegetable waxes which are of interest to the perfume maker will be found discussed in Chapter 30.

oils to edible solids; particularly, in the United States, for the hydrogenation of cottonseed oil, but it has been extended considerably, for instance to the hardening of fish oils which are then made into soaps.

The commercial procedure is to suspend finely divided nickel in the oil heated to 250° to 300° F. (121° to 149° C.) and blow in hydrogen gas. Nickel gauze may be used instead of the powder. Agitation of the oil by rotating arms is customary. The nickel is used in amounts of 0.5 to 1 per cent of the weight of the oil. It may be introduced in the form of its oxide, which is soon reduced to the metal by the gas, but the previous reduction in a separate vessel is the better procedure, for among other reasons the metal may be filtered out almost completely after the reaction, while in the cases when the oxide is used, an appreciable amount remains dissolved in the oil, presumably in the form of a soap. Palladium is a far more effective catalyzer; 1 part in 100,000 parts of oil is sufficient, and the reaction proceeds at a lower temperature, and in less time. In spite of these advantages palladium is rarely used, because of its high cost.

The hydrogen gas must be pure,[15] and should be introduced at the same rate at which it is absorbed.

Any glyceride which has unsaturation may be hydrogenated. For example, glycero-trioleate, a liquid, is thus changed to glycero-tristearate, a solid. The hydrogenation may be continued until all of the unsaturation has been relieved; the result is a fat which melts too high, for an edible fat should melt below the body temperature. It has become the practice to hydrogenate only far enough to form a fat of the desired melting point, rather than mix the harder product with fresh oil. The progress of the reaction is followed by samples drawn off at intervals.

$$
\begin{array}{ll}
CH_2-O-OC \cdot H_{33}C_{17} & CH_2-O-OC \cdot H_{35}C_{17} \\
CH-O-OC \cdot H_{33}C_{17} + 6H = CH-O-OC \cdot H_{35}C_{17} \\
CH_2-O-OC \cdot H_{33}C_{17} & CH_2-O-OC \cdot H_{35}C_{17} \\
\textit{glycero-trioleate} & \textit{glycero-tristearate} \\
\text{(a liquid)} & \text{(a solid)}
\end{array}
$$
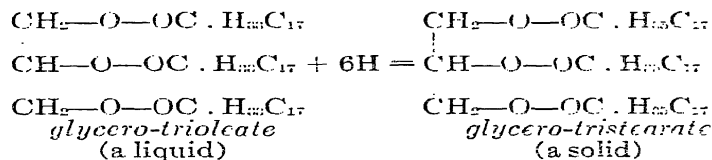
When the catalyst is "supported," the support is generally diatomaceous earth. Its preparation consists of adding 15 to 20 per cent of the earth to a nickel sulfate solution, stirring, and at the same time precipitating the nickel as oxide by a solution of sodium carbonate. The precipitate is washed, filtered dry, and reduced with hydrogen at as low a temperature as possible (300° to 400° C. or 572° to 752° F.). The finished catalyst should contain 20 to 25 per cent Ni. At once on leaving the reducing furnace, the nickel catalyst is placed under oil, to preserve its activity.

The "wet" reduction, illustrated in Figure 171, which shows a complete oil hydrogenating plant, is still better, and consists of suspending nickel carbonate or nickel formate in the oil, heating and agitating, with

[15] Chapter 19.

simultaneous entry of hydrogen. The temperature is 225° to 250° C. (427° to 482° F.).

The catalyst is then pumped to the converter, in which the charge of oil has been brought to reaction temperature by a steam coil. The reaction temperature depends upon the purity of the hydrogen and the activity of the catalyst. It is usually 120° to 176° C. (250° to 350° F.). Hydrogen is admitted through a perforated pipe at the bottom of the
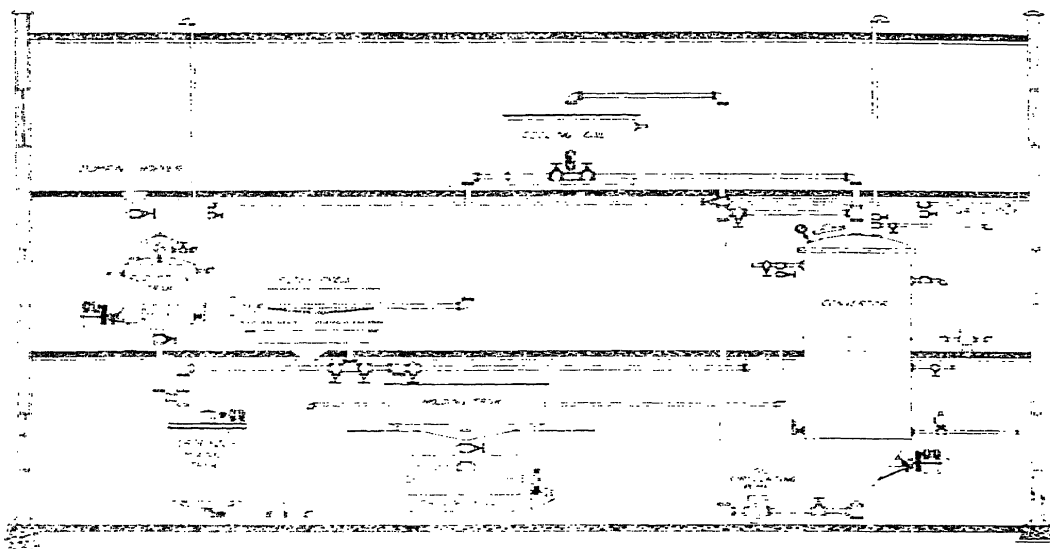
FIGURE 171.—A plant for the hydrogenation of oils to fats, including: catalyzer reduction tank, catalyzer mixing tank, converter with liquor circulation and with agitator, filter press, cooling coil, holding tank and chilling roll. (Courtesy of Wurster and Sanger, Inc., Chicago.)

converter, so that numerous fine streams are formed. The unused gas at the top of the vessel is pumped away and recirculated through the bottom pipe, with fresh gas, and a part of the liquid is pumped from the bottom of the converter to a spray coil at the top of the converter. A high speed propeller at the base of the converter agitates the oil. The necessary intimate mixing necessary for rapid reaction is thus insured.

The hydrogenating reaction is exothermic for all oils, so that after it is started, a part of the oil must be cooled by passing it through an outside cooling coil.

After the reduction has proceeded to the desired point (conveniently followed with a refractometer), the charge is cooled somewhat, filter pressed, and in some cases deodorized by passing carbon dioxide into the melted fat, heated to 130° C. (266° F.), for an hour, or by some other method. On cooling, it is now a soft solid, a semi-synthetic fat. The catalyst is mixed with oil and used over again.

If completely hydrogenated, cottonseed oil would melt at 62° C.

(143° F.); for making the edible fat, hydrogenation is stopped when a melting point of 34° to 35° C. (93° to 95° F.) has been reached.

A continuous method for hydrogenation has been devised by Bolton and Lush,[16] in which the catalyst consists of nickel turnings or wire held in a wire basket which nearly fills the hydrogenator. The warmed oil enters at the top, the hydrogen gas at the bottom, with recirculation. Hydrogenation with the corresponding hardening take place, and its degree may be controlled by altering the rate of oil flow; feeding slowly will give high hardening, feeding fast will give only slight hardening. Among other advantageous features this process offers is the one of short period of heating, which favors a pale color.

The total amount of vegetable hydrogenated in 1935 in the United States was 748,390,732 pounds (Bureau of the Census).

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Formerly the materials used by the perfume maker were entirely the natural products; to-day, these are supplemented by a number of synthetic products. The preparation of the synthetic substances and improved methods for the extraction of natural substances are the contributions of chemical science to the perfume industry. The work of the perfume maker, which consists of the proper blending of odoriferous substances, requires artistic ability as well as scientific knowledge.

Chapter 30 *

Essential Oils, Perfume Sundries, Flavors, Pharmaceuticals

Perfumes are made from essential oils, the odoriferous principle of a number of plants. Usually a number of oils are blended together, in alcohol solution, and a fixative is added in order to render more lasting the odor which otherwise would be fugitive. A perfume may therefore be said to consist of three parts: the odoriferous part, the fixative part, and the diluent. The function of the diluent, practically always ethyl alcohol, is to reduce the concentration of the blended oils to an odor strength similar to that of the flower. The number of typical fixatives

TABLE 62.—*Essential Oils with Their Country of Origin.*

Oil lavender fleur	from the flower, hence "flower oil"	France
Oil ylang ylang Bourbon†	from the flower	Réunion
Oil of rose	" "	Bulgaria and France
Oil of patchouli	from the leaf	Singapore
Oil eucalyptus	" " "	Spain and Australia
Oil geranium Bourbon	from the herb	Bourbon Islands, Algeria and France
Oil rosemary	" " "	Spain and France
Oil thyme red	" " "	Spain, France and Syria
Oil bergamot	from the fruit	So. Italy
Oil orange and oil lemon	" " "	So. Italy, California, West Indies and Africa
Oil fennel	from the seed	Middle Europe
Oil anise	" "	China, Spain, Russia
Oil caraway	" " "	Europe, North Africa
Oil bois de rose	from the wood	French Guiana and Brazil
Oil guaiac wood	" " "	
Oil vetivert	from the root	Bourbon Island
Oil of orris (a solid)	" " "	No. Italy and So. France
Oil olibanum	from the gum	Arabia, Levant
Oil cinnamon Ceylon	from the bark	Ceylon
Oil citronelle Java	from the grass	Java
Oil palmarosa Turkey	" " "	Turkey

† Old name for the French possession Réunion.

* In collaboration with Mr. Earl Booth, chemist-perfumer, Larkin Company, Buffalo, N. Y.

is small; the number of essential oils, very large. The synthetic substances are usually pure chemical substances, whereas the essential oils are natural mixtures. Some synthetics are artificial reproductions of natural substances, others give entirely new odors.

Essential oils are obtained not only from the flower, but also from the leaves, roots, and seeds of plants, and from the roots and barks of trees. Table 62 gives a number of examples, with the countries of origin.

Essential oils are used not only for perfumes proper, but also for perfuming soaps; for that purpose they must be lower in cost. As a rule an essentail oil costing less than $5 a pound may be used for soaps. For perfumes proper, there is no price limit, except that for the less-expensive perfumes, the cheaper raw materials must be used; many of these are synthetics. Examples of synthetics follow:

Class	Samples
acids	Benzoic acid, Phenyl acetic acid (solids).
alcohols	Linalool, Terpineol (liquids)
aldehydes	Benzaldehyde, Phenyl acetic aldehyde (liquids)
esters	Amyl salicylate, Benzyl acetate (liquids)
ether	Di-phenyl oxide (solid)
ketone	Ionone α and β (liquids)

Among the synthetics, certain ones are made from benzene, toluene, phenol, or other coal-tar products; thus benzoic acid and benzaldehyde from toluene, diphenyl oxide from phenol. These may be said to be true synthetics. Others are semi-synthetic only, for they are made from a natural plant product; thus ionone is made from citral, which is isolated from lemon-grass oil. If a constituent of a natural oil is isolated, by distillation for instance, and used as such, it is called an isolate; thus geraniol is an isolate from citronella oil.

A number of essential oils are used as flavors as well as perfumes, for instance the oils of lemon, bergamot, and orange (peel). Vanillin, oil angelica, and coriander oil are used both for flavoring and for perfumes. Another example is oil of peppermint which has a further interest in that on cooling it,[1] large crystals of menthol separate, much used in dental pastes as a flavor, and also as a pharmaceutical. Formerly the pharmaceuticals were chiefly plant extracts; now they include a large group of manufactured chemicals, of constantly increasing number and importance.

ESSENTIAL OILS

Essential oils are obtained by volatile solvent extraction, by steam distillation, by expression, and by enfleurage.

The extraction by means of volatile solvents is of wide application, and is the more important method for fine oils. The practice in southern France for oil of rose may serve as example. The rose cultivated in Provence is chiefly *Rosa centifolia*, a pink rose. The petals are placed on trays in copper vessels and percolated with low-boiling petroleum ether;

[1] Japanese peppermint oil is rich in menthol.

the waxes present are dissolved as well as the oil. The solvent is removed in stills under reduced pressure so that very gentle heat only is required, and there is left a semi-solid residue, called concrete, and containing about half its weight of oil. The rose concrete is next dissolved in warm alcohol, and this solution is cooled. The waxes separate and may be removed by filtration. The filtrate is placed in small copper stills, the alcohol removed by distillation, and there is left the pure oil of rose, called rose absolute No. 1. The waxes may be washed again, giving a solution called rose extract. The amount of oil in one rose blossom is very small; to produce 1 ounce of rose absolute, some 60,000 blossoms are required. By weight the yield is about 0.1 per cent. The price is about $10 an ounce, and this is not too dear considering the labor involved in growing and preparing the many blossoms required.

The best known concretes are rose, jasmin, tuberose, orange flower, cassie (a small yellow flower), and rose lavender; the corresponding absolute oils are made by alcoholic extraction. Concrete violette de Parme, formerly so well known, is now extinct in perfumery. Some perfumers prefer to buy the concrete, and make their own alcoholic extracts of the same without reducing it to the absolute form.

The most expensive of the absolute oils is violet, which brings $75 an ounce if free from any addition; this is almost too dear, and violet perfumes are made chiefly from methyl ionone, a semi-synthetic.

In order to obtain the oil by distillation, the blossom, herb, or chipped root is placed with water in a still with goose-neck, and heated by a steam coil, or steam jacket, or by live steam introduced below the false bottom on which the material rests. For peppermint, which is a good example, the distillate may be cooled in a condenser made of ordinary conductor pipes such as are used for rain drainage on dwellings; the cooling is by cold water. The first home-made installation has been replaced in most cases by modern equipment. Two layers form, the oil being the upper one; the water layer is wasted, in this case. In the case of rose blossoms, however, the water retains a certain amount of oil in solution, and is then carefully preserved and sold as such, for the demand is considerable. The proportion of rose water to oil may be reduced if desired by returning it to the still so that new water need not be introduced; in such cases a steam jacket would be the source of heat. Bulgarian otto of rose is a distillation product and is the ordinary otto of commerce; real French otto of rose is rarely seen at the present time because the production cost is less in Bulgaria. The blossoms used in Bulgaria are the *Rosa Damascena*, a red rose.

There may be a combination of odors in the distillation itself with good results; thus geranium (the whole plant) may be distilled by itself, giving geranium oil; or rose petals may be added to geranium oil made the previous fall, and the two distilled together, with the production of oil of geranium sur roses, possessing a superior odor.

Steam distillation is suitable for the production of the oil because the essential oils are either insoluble, or very slightly soluble in water.

The industry is seasonal, so that every year the raiser of peppermint or spearmint uses the still for two or three weeks; a simple installation is economically correct. For many oils, the dried leaves or roots, produced in one place, may be shipped to a center for extraction, and in that way material provided for constant operation; in such centers very elaborate machinery may be provided. The most important of these centers is Grasse, near Nice; it is surrounded by flower-producing areas, and in addition receives imported materials such as patchouli leaves and vetivert roots from India, and orris root from Italy (Florence). The important products at Grasse are neroli oil from the bitter orange blossom, jasmin, verbena, narcissus, jonquil, orris, tuberose, cassie, and violet; these are not excelled by products produced elsewhere. French lavender oil is the main lavender oil; English lavender oil formerly was of importance, but is now practically extinct. Material reaching the market labeled English lavender oil is usually a blend of French oils. Steam distillation is the chief method of producing oils, thus, orange blossom, verbena, orris and lavender; the second method is extraction by volatile solvents, already presented.

Other products of steam distillation are oil of cloves, cinnamon oil from the bark (very little), coriander from the crushed seed, guaiac from the wood, found in India; oil bois de rose, which has no relation to the rose blossom or its oil but is obtained from a laurel in French Guiana; oil vetivert; citronella oil from Java (best) and Ceylon; and geranium oils.

The peel of the orange, the bergamot, a small citrus fruit on the order of the lime, and the lemon, are pressed, both by hand and by machinery, in order to obtain the oil they contain; there is also a distilled oil of these peels, of inferior value. The oils have a high content of terpenes and steropton (steropton is the name given to any wax which separates from an oil on standing). In order to concentrate the citral, the characteristic odoriferous part in the case of lemon oil, the terpenes are removed by distillation in a steam-jacketed vacuum still (not by directly introduced steam), and the residual oil is then terpeneless oil of lemon, or orange. The distillate serves as diluent for inferior quality or synthetic oils. It is because of the high terpene content (about two-thirds) of these oils that on standing the odor changes. Presumably the terpenes polymerize, gaining in odor, until the odor of the citral is overbalanced; the spoiled oil is termed rancid. Chemically pure citral is mentioned in the next division.

In enfleurage by the cold process, the flower or the separate petals are pressed against warm fat, a fine grade of benzoinated lard, spread on glass plates 1 foot wide by 2 feet long, fitted with wooden frames. Both sides of the glass are greased; petals are placed on the upper side only, and the frames piled on each other, so that the lower side touches the petals on the glass of the frame below. After a day the petals are removed by hand, or by a brush, fresh petals spread on, and this repeated until the lard has the maximum amount of oil it can absorb. The lard is then scraped into containers and preserved in cooled cellars; at this

stage the product is pomade, formerly used as such. From the pomade, the absolute oil is obtained by extraction with alcohol, followed by a distillation to remove the solvent, and in order to distinguish such absolute from that obtained by the volatile solvent method, it is called "absolute pomade," thus Jasmin Absolute Pomade. This process is used less than formerly; much labor is involved, and the fat tends to turn rancid; efforts to substitute soft paraffin waxes have not been successful, because their absorption power is low. A modification of enfleurage is to macerate the rose blossoms with warm fat, filtering from the blossoms, and cooling; the resulting pomade may be extracted for the oil by alcohol. The alcohol is recovered. Rose and orange blossom pomades are made by the hot process, jasmin and tuberose pomades by the cold enfleurage process.

SYNTHETICS, SEMI-SYNTHETICS, AND ISOLATES

Benzaldehyde is made by chlorinating toluene, and boiling with caustic; its odor is similar to that of bitter almond oil. Nitrobenzene[2] is called oil of mirbane, and has a penetrating odor; its use is chiefly for soaps and for shoe polish. Dimethyl hydroquinone is a white solid, valuable for synthetic narcissus perfumes. Cinnamic aldehyde has been sold under the name of Cassia oil redistilled; it may indeed be isolated from cassia, but like the other substances in this paragraph, it is made synthetically with great ease and at low cost.

The chemical relation between a number of synthetics is shown below:

```
        Chlorine                                    Toluene
        └── ──────Benzyl chloride──── ──┘
──────────────────────────────────────────────────────────────

Benzyl alcohol              Benzaldehyde              Benzyl cyanide
      ↓                          ↓                          ↓
  Benzyl acetate           Cinnamic aldehyde          Phenyl acetic acid
                                 ↓                          ↓
                           Cinnamic alcohol           Phenyl ethyl alcohol
```
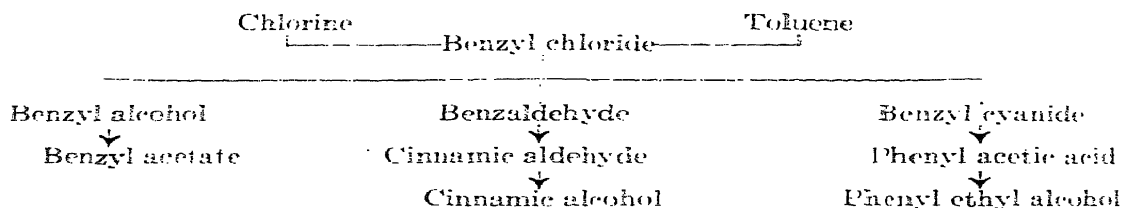
Vanillin[3] is a semi-synthetic; it is made (1) from iso-eugenol which itself is made from eugenol, an isolate from oil of cloves or cinnamon leaf oil; (2) from guaiacol fractionated from the phenols in coal-tar; (3) from iso-saffrole, itself obtained from brown camphor oil. Vanillin is a white solid, and in this form is used by the perfumer, rather than in the form of the extract from the vanilla bean. The odor of vanillin is delicate; vanillin forms part of a surprisingly large number of perfume formulas. Piperonal[4] is a solid aldehyde, sold under the name of heliotropin. Coumarin[5] is made synthetically, although it occurs naturally, for instance in tonka beans; it is a white solid prepared from salicyl aldehyde; its odor is sharper and more penetrating than that of vanilla. The most remarkable of the semi-synthetics are the ionones,[6] two ketone isomers differing only in the position of a double bond (unsaturation); α-ionone is about

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[2] Chapter 27.

$8 a pound, β-ionone about $6.   The ionones are made by condensing citral with acetone, and boiling with dilute sulfuric acid.   Citral is a liquid of formula $(CH_3)_2 \cdot C:CH \cdot CH_2 \cdot CH \cdot C(CH_3):CH \cdot CHO$, and is isolated from lemon-grass oil by forming the sodium bisulfite addition compound; pure citral is $2 a pound.   The two isomeric ionones are separated by their sodium bisulfite compounds, which differ in solubility (the α-ionone compound is less soluble).   Alpha-ionone with suitable admixtures produces a true violet odor.   All the substances in this paragraph except coumarin are semi-synthetics.

Geraniol is an important substance, an example of an isolate; it is obtained from palmarosa oil or citronella oil, and serves to imitate the rose odor.

From lemon grass oil, a number of valuable semi-synthetics are obtained:

Oil lemon grass

| by distillation | by NaHSO₃ and distillation | by methyl-ethyl-ketone condensation | by acetone condensation |

by distillation → Citral, technical

by $NaHSO_3$ and distillation → Citral 100% C. P.

by methyl-ethyl-ketone condensation → Pseudo methyl ionone → Methyl ionone

by acetone condensation → Pseudo-ionones → Inone crude

by rectification Ionone standard → Ionone 100% α and β

by $NaHSO_3$ → Inone alpha

[3] Vanillin (solid)   HO ... $\overset{H}{C}=O$ ... OCH_3

[4] Piperonal (solid) $\begin{smallmatrix} O \\ O \end{smallmatrix}>CH_2$ ... $H-C=O$

[5] Coumarin (solid) $\overset{H}{C}=CH$ ... $O-C=O$

[6] $CH_3 \quad CH_3$
$H_2C \overset{C\,H}{} C-CH=CH.CO.CH_3$
$H_2C \quad C.CH_3$
$\overset{C}{H}$
α-ionone (liquid)

$CH_3 \quad CH_3$
$H_2C \overset{C}{} C-CH=CH.CO.CH_3$
$H_2C \quad C.CH_3$
$\overset{C}{H_2}$
β-ionone (liquid)

A new method of preparing a number of semi-synthetics for their odor and flavor is the cracking of castor oil, with subsequent treatment of the cracked distillate.[7]

Castor oil
by cracking

Oenanthol	*with methyl heptin carbonate*		Undecylinic acid		
with benzaldehyde	Artificial green (violet leaf odor)	Aldehyde C_9	Aldehyde C_{11} saturated and C_{11} unsaturated	Gamma undecalactone (peach odor)
Amyl cinnamic aldehyde (jasmin odor)					
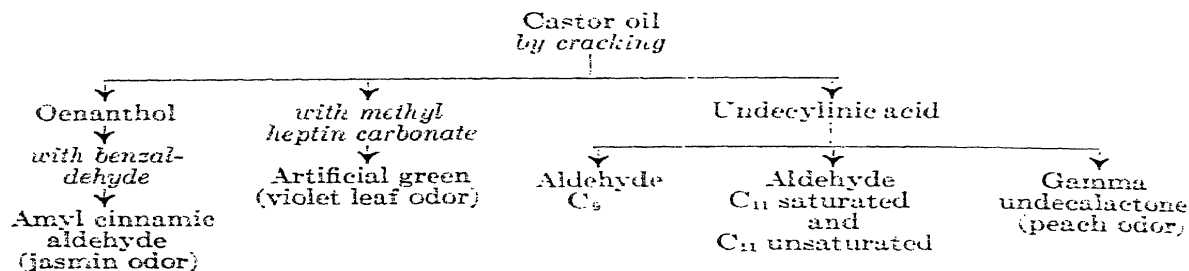
PERFUME SUNDRIES—FIXATIVES—RESIN OILS

Under perfume sundries any substance is included which enters into a formula for a perfume without directly contributing to its odor. The fixative serves primarily to render the odor more lasting; it is chosen so that it blends well with the oil odor. Three substances have been used for many years past and are still the most important fixatives; these are ambergris, musk, and civet.

Ambergris is a calculus in the stomach of the sperm whale which has formed around a sharp foreign substance such as the beak of the squid, and which is excreted and found washed ashore; it may be also cut from the stomach of a whale caught for its oil. Ambergris is dissolved in alcohol, and is used in tincture form. Its odor is earthy, and its fixative power remarkably great; it is used for the floral perfumes.

Musk is the preputial follicle of the musk deer, found in Tibet and in Manchuria; it has not been possible to raise the deer in captivity. The musk pod is situated at the stomach of the deer; each pod yields about an ounce of musk, worth about $22. The odor of crude musk is disagreeable, but the alcoholic solution after aging several months is not unpleasant. Musk is the fixative for the so-called oriental perfumes (heavy perfumes.)

Civet is obtained from the civet cat, in Abyssinia; crude it is also disagreeable; in the form of aged alcoholic solution, it is used as musk is. Frequently both musk and civet are used in one perfume.

Artificial musk is a synthetic product, which has fixative value: the first was musk xylene; the best one at present is musk ambrette, dinitrobutyl-metacresol-methylether, made from cresol. Among the essential oils, vetivert, orris, and some others sometimes perform the function of fixatives.

Odoriferous resin oils and oleo-resins are important mainly for their odor, only secondarily as fixatives. Oleo-resin of olibanum is made from a gum-resin obtained by incisions in the bark of pine growing in

[7] For definition of cracking compare the chapter on petroleum.

the Levant (Asia Minor), the *Boswellia Carterii*. The gum-resin is extracted with alcohol and filtered from the non-solubles (gums); the alcohol of the solution is distilled and there is left a viscous mass, the oleo-resin, with the odor of church incense. By distilling the gum-resin itself, oil olibanum is obtained. Olibanum is the frankincense of the ancients. Labdanum, found on the leaves and stem of a low plant, yields similarly, oil labdanum. Liquid amber also belongs to this class of fixatives.

PERFUMES

Perfumes contain from 2 per cent (weak) to 10 per cent (very strong) odoriferous matter including fixatives; the remainder is alcohol (ethyl). The floral perfumes imitate single flowers, while fancy or bouquet perfumes do not. As example for a simple perfume formula, of the floral type, the following is given:

Type of Formula for Rose Perfume—Highest Type.

	Grams
Oil of rose (the natural floral oil, the otto)	10
Rose absolute (floral oil, from the concrete)	10
Geraniol (an isolate)	25
Phenylethyl-alcohol (a synthetic)	20
Oil of geranium (an essential oil)	10
Alpha-ionone (semi-synthetic)	15
Resin of labdanum (resin oil)	5
Tincture of musk	5
Alcohol (90%)	900

This would be a strong perfume of fine quality.

Examples of fancy perfumes are Chypre and Ambre, both of the oriental type.

TOILET WATERS

Toilet waters form a class of perfumes by themselves; they are made up with alcohol chiefly; that they are nevertheless called waters is because the French word for water is frequently used for "liquids." [8] The best-known toilet water is Eau de Cologne; the original formula required a distillation, as indicated in the following one, a close approximation:

Bergamot oil	10 cc.
Lemon oil	15 cc.
Lime oil	5 cc.
Orris root	20 grams
Alcohol (90%)	480 cc.
Water	60 cc.

This is permitted to stand 24 hours, and is then distilled; to 480 cc. of the distillate there are added

Neroli oil bigarade	3.0 cc.
Rosemary oil	0.5 cc.
Lavender oil French	0.5 cc.
Oil of thyme	0.5 cc.

[8] Compare *eau de vie*, meaning—whiskey or brandy.

The whole is matured one month. The odor is refreshing, not very lasting. Eau de Cologne is now frequently made without a distillation. Lavender water is a favorite in England; a simple formula is:

Lavender oil French	20 cc.
Bergamot oil	10 cc.
Sandalwood oil	1 cc.
Civet extract (5%)	5 cc.
Orris resin	4 grams
Alcohol (90%) to make	1000 cc.

Florida water, an American toilet water, contains orange-flower water and cinnamic aldehyde, which give it its distinctive note.

FLAVORS

Flavors are used for cooking, for candy, chewing gums, beverages, syrups, dental pastes, and medicines. Oil of lemon, of orange, and of lime have been described; they are obtained by expression, and may be freed from the terpenes. Peppermint is made into crême de menthe (Italy). Vanilla extract is perhaps the best-known flavor, and used for numerous purposes. It is made from the vanilla bean, after it has been cured in order to develop the vanillin content, by extraction with alcohol. The American practice is as follows: 50 pounds of Mexican vanilla beans and 50 pounds of Réunion beans are chipped fine in an automatic cutter, and placed in a "batteuse," a cylindrical extractor of steel, fitted with a stirrer. Fifty per cent alcohol is added, in the cold, and stirred for an hour; the extract is run off, and three further extractions made in the same way. The extracted mass is pressed in a wine press and discarded. All four extracts are combined to give the finished material. The amount of 50 per cent alcohol is such that the beans form 10 per cent by weight of the solvent taken. The extract is colored brown by some of the resin which is dissolved.[9]

The use of synthetics as flavoring agents is on the increase, as will be seen from the following short list. Methyl anthranilate gives the odor of grapes; ethyl butyrate is basically the odor of rum; saffrole, from brown camphor oil, is an artificial sassafras, and is used in root beers, candies, and "herb tonics." Cinnamic aldehyde replaces cinnamon oil, methyl salicylate oil of wintergreen. Frequently used also is benzaldehyde F.F.C. (free from chlorine) as "oil of bitter almond, artificial."

Diacetyl $CH_3.CO.CO.CH_3$, a yellow, somewhat viscous liquid, and diacetyl carbinol, a white, thin liquid, are the chief odoriferous flavor of butter made from sour cream, and are produced by the action of a microorganism. These two substances are now prepared on the large scale, by the action of the same organisms, in special cultures, and are available for flavoring, in cases not prohibited by the pure food laws.

[9] The fresh vanilla bean is green; in size it may be as long as 10 inches; the dried bean is brown. Vanilla beans are shipped tied in bundles of about 30 beans selected of one size. The beans from Réunion, and others, often have a bloom of vanillin on their surface.

INDUSTRIAL PERFUMERY

Odoriferous substances are being used more and more in the general industries and manufacturing, sometimes to render goods more attractive, more often in order to cover or mask a disagreeable odor inherent in the goods. Examples are: Leather gloves, shoes and handbags, stockings, cotton pads, stationery, wall board (to imitate cedar), lacquer, varnishes and leather dopes, inks, cameras, knit goods, sweaters, and tickings, tobacco, rubber, lubricating oils and greases, kerosene fly and moth sprays, disinfectants including para-dichlorobenzene, undertakers' specialties, formaldehyde, shoe and metal polishes, floor sweeping compounds. Perfumes are often used in ventilating fans, theater sprays and incense. Depending upon the use, the price of the perfume material used will vary from a few cents a pound to $1 a pound.

PHARMACEUTICALS

Any substance used for therapeutic purposes may be classed as a pharmaceutical, so that the list is long. Formerly, pharmaceuticals were chiefly extracted from crude drugs of vegetable origin, and to a lesser extent, materials of animal origin (cod-liver oil). To-day the natural pharmaceuticals are supplemented by synthetic products, examples of which are given below; at the same time, new successes in materials of vegetable or animal origin are of late date, thus insulin, from the pancreas of the steer, for diabetic patients. Of the strictly synthetic products, arsphenamine (salvarsan), the specific for syphilis, is of first importance; its modern form is neosalvarsan,[9a] stabler in air. Quinine sulfate from the bark of the cinchona tree, Peru and Bolivia, is an antipyretic; it is supplemented by the synthetics acetanilide, used for headache powders (bromo-seltzer), and acetylsalicylic acid (aspirin). The narcotic morphine sulfate, the local anesthetic cocaine hydrochloride, the mydriatic (pupil-dilating) atropine sulfate are natural products. Cocaine is now supplemented by synthetic substances, such as procaine hydrochloride (novocaine), and several other like products, used in dental surgery. The laxatives are still essentially of vegetable origin, thus the cascara sagrada bark extract and castor oil; of the synthetic laxatives, phenolphthalein is

9a

salvarsan

neosalvarsan
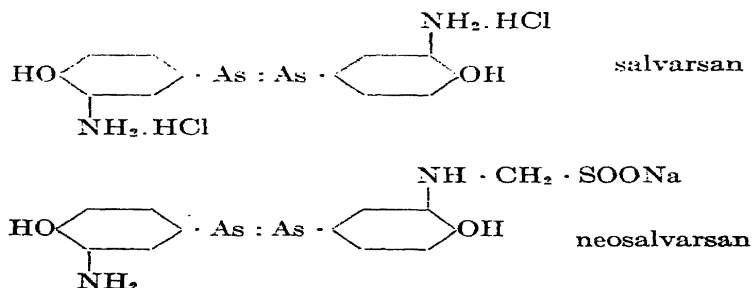
successfully prescribed. Epsom salt is described in Chapter 12. The important anesthetic liquids, chloroform and ether, which have revolutionized surgery, robbing operations of their terrors, and removing the resistance of the conscious patient, are synthetics of comparatively simple manufacture. As they are both made from ethyl alcohol they might be called semi-synthetics since alcohol is a fermentation product; alcohol may be made from acetylene, when it would be strictly synthetic. The hypnotic paraldehyde is polymerized acetaldehyde, from the distillation of wood; hence it may be called a semi-synthetic. Veronal, a sleeping powder, and saccharin, a sweet non-sugar, are true synthetics. Phenol, formaldehyde, hydrogen peroxide, and iodoform are described in other chapters, radium in Chapter 50.

Ether is made mainly by the dehydration of ethyl alcohol by sulfuric acid; the process is continuous. The sulfuric acid mixed with a certain amount of alcohol is brought to the temperature of 140° C. in a lead-lined steel boiler by means of steam in a closed lead coil; alcohol is vaporized in a separate vessel and the vapor sent through the acid-alcohol mixture in the still.[10] There passes out a mixture of ether, alcohol, and water, in vapor form, and these are separated in a column still. The water passes out at the bottom. Alcohol, containing some ether and some water (5 per cent), is removed in vapor form half-way up the column, is condensed and used over again in the vaporizer. At the top of the rectifier, ether vapors pass out and are condensed in a separate condenser; such ether contains a small amount of water and alcohol. Sulfur compounds are removed previously, by passing the mixed vapors from the still through a dilute caustic solution. The efficiency of the process is high, about 94 per cent. The reactions are:

$$C_2H_5OH + H_2SO_4 = C_2H_5.HSO_4 + H_2O$$
$$\textit{ethyl-sulfuric acid}$$

$$C_2H_5OH + C_2H_5.HSO_4 = C_2H_5.O.C_2H_5 + H_2SO_4$$
$$\textit{ether}$$
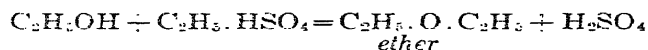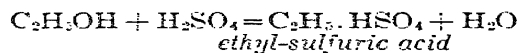
The sulfuric acid is regenerated; instead of sulfuric acid, benzene-sulfonic acid has been proposed. A temperature of 128° C. is preferred in a British plant.[11]

Ether is lighter than water and forms an upper layer; it boils at 34.5° C. (94° F.), while chloroform boils at 61° C. Ether is widely used as an anesthetic and as a solvent. Of the medicinal grade, 7.97 million pounds were made in 1935 (U. S.), valued at 18 cents a pound.

Chloroform is more rapid in its anesthetic action than ether; it is more depressing to the heart action. Both are being supplemented more and more by nitrous oxide mixed with oxygen, even in major operations. The anesthesia is begun with ether, for instance, and then continued with

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[10] Or an intermediate tower with quartz packing may be used in which the regenerated acid mixes with the alcohol, and the mixture overflows in the still proper; U. S. Patent 1,328,258.

[11] "Organic medicinal chemicals," Barrowcliff and Carr, New York, D. Van Nostrand Co., 1920, p. 128.

nitrous oxide applied at intervals as may be necessary to keep the patient unconscious.

Cocaine hydrochloride is extracted from coca leaves, of the *erythroxylon coca* and related plants, found in Ceylon, Java, Peru, and Bolivia; the content of cocaine base in the leaves varies from 0.7 to 2 per cent. The extraction is chiefly by a mixture of aqueous soda ash and petroleum ether, used warm and constantly agitated in a vessel with stirrer. The alkaloid as the base dissolves in the ether, and is precipitated by hydrochloric acid, as the crude hydrochloride; this is filtered, dried, and sent to the refiners in the consuming countries.

Acetyl-salicylic acid, sold in part under the name of aspirin, is made by dissolving salicylic acid [12] in glacial acetic acid, in an earthenware-lined vessel, and adding an excess of acetyl chloride. The vessel or still is jacketed and the contents are heated until the reaction starts, when the steam may be turned off, for the reaction is exothermic. Hydrogen chloride passes out through a worm which condenses the acetyl chloride carried out, and then reaches a small tower where it is absorbed in water. At the end of the action, steam is sent through the jacket and the remaining acetyl chloride distilled. The crude acetyl-salicylic acid is left in the still and is purified by solution in alcohol and precipitation by water.

In 1934, 3,884,419 pounds of medicinal salicylic acid and salicylates were produced, with an average value of 56 cents a pound.

Procaine is made from para-aminobenzoic acid, by forming the di-ethylamino-ethyl ester; the resulting base is insoluble in water, but its hydrochloride is freely soluble. It is used chiefly in the latter form. The successful introduction of procaine hydrochloride as a local anesthetic replacing cocaine and partly sold under the name of novocaine, has led to the preparation of a large number of similar esters, and also of substances with different structures. Like all materials used in pharmacies, a prescribed standard of purity must be reached. [13]

Total medicinals of coal tar origin produced in 1935 were 10,022,667 pounds, of which 8,949,747 pounds were sold at an average price of 94 cents a pound; the sales of medicinals of non-coal tar origin were 568,839 pounds, with an average value of $2.36 a pound. (*U. S. Tariff Commission Report* 115).

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[12] Chapter 27.

[13] These standards are listed in the U. S. Pharmacopœia, 10th edition (1926), obtainable from J. B. Lippincott, Philadelphia. The newer remedies are listed separately, in "New and Non-official Remedies," published yearly by the American Medical Association, 535 No. Dearborn Street, Chicago, Ill.

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That the preparation of protective coatings for steel and lumber is an important industrial activity is apparent when it is considered that the interior and exterior of buildings, railway and motor cars, the bottom as well as the superstructure of ships, and the cables, girders, and arches of bridges are so treated. The chemist-technologist has invaded this field and made important contributions in the form of improvements and discoveries.

Chapter 31

Pigments, Paints, Varnishes, Lacquers, Printing Ink

The pigment industry is usually thought of as associated with paints, but it is really a separate industry, which should be considered by itself, for although a considerable tonnage is mined or manufactured for use in paints, another part about as great is consumed in making rubber goods, linoleums, oil cloth and artificial leather, plastics, ceramics, and other articles.

Of the white pigments, white lead and zinc oxide are about equal in importance; they are manufactured in greater quantities than any other pigments; the yearly production in the United States for the two is over 185,000 tons. Among the white pigments, lithopone ranks first with 160,000 tons, with blanc fixe next and Titanox trailing. Of manufactured red pigments rouge, an iron oxide, is the most important; brown and red ochres and sienna are natural iron oxides. Red lead is used in considerable quantities. Lamp black and carbon black are the important black pigments with graphite a poor third. Ultramarine (blue), cinnabar (red), lead chromate (yellow), chrome oxide (green) and many others are used for color to a great extent, metallic salts of organic dyes to a lesser extent. For ceramics metallic oxides are in demand. Other uses of pigments are discussed in the appropriate places; the rôle of pigments in paints, enamels, lacquers, and printing inks will be discussed in this chapter.

WHITE LEAD

White lead is a basic carbonate of lead, that is, a carbonate combined with the hydroxide; its formula is $2PbCO_3.Pb(OH)_2$ but the variations are considerable; it is better to remember it merely as a basic carbonate. It is made, in one process, by corroding lead in the form of cast buckles by the vapors of acetic acid and water, in the presence of carbon dioxide emanating from fermenting tan-bark; lead acetate forms first, and this is transformed by the carbon dioxide and moisture partly into carbonate, and partly into hydroxide. The buckles are placed in small earthenware crocks 8 inches in diameter and 10 inches high, in which a pint of 28 per cent acetic acid has been poured; the buckles lie over the acid, resting on a small shoulder in the inner wall of the crock. A layer of these

crocks is placed in a thick bed of spent tan-bark, then covered by boards, over which more tan-bark is shoveled, and another tier of crocks is set in that. This is repeated till 10 or more tiers are made ready. Some ventilation to the center is provided by a stack-like opening in the middle. The room is then closed. Fermentation proceeds and the temperature rises perhaps to 70° C.; the pots remain undisturbed for three months. After that time they are unpacked, and the buckles, now white, lifted out, crushed free from any uncorroded center, and ground dry or wet. This is the Dutch process. It requires much hand labor, and is slow; but the quality of its product (covering power) is held to justify its continuance. Extremely pure lead is required for this process, otherwise the corrosion does not proceed far enough.

A process which needs no tan bark and thus avoids an occasional contamination, is the Carter process,[1] in which melted lead is first atomized by superheated steam very much as oil would be in an oil burner, then placed in wooden cylinders lying on their sides and rotated slowly. At intervals dilute acetic acid and carbon dioxide from a coke fire are fed in with some air: after 15 days, the lead is corroded, and has become white lead.

In the French process, little time is required: litharge (PbO) is dissolved as a basic lead acetate in acetic acid, and carbon dioxide (fire gases) pumped into the solution: the basic carbonate precipitates and is filtered off. The lead salts remaining in solution are not lost, for the filtrate is used in making ready with the next batch.

In the Rowley process no acetic acid is used; the atomized lead in suspension in water is exposed to warm air, when the hydroxide forms: carbon dioxide is pumped in for a certain period and white lead of good covering power forms.

When grinding dry, dust forms, and this is a source of danger because white lead is poisonous; for that reason the grinding is usually done wet. The suspended solid is thickened by settling, giving "pulp lead": this need not be dried, if the pigment is intended for paint, so that an oil paste would be suitable. By mixing the pulp with linseed oil, the latter displaces the water which rises to form an upper layer, readily run off; the custom is to make a paste containing 92 per cent white lead and 8 per cent raw linseed oil. If the dry pigment is required, grinding dry, for the Dutch process at least, is the easiest way.

Sublimed White Lead (Sulfate). In any process for white lead, the metal or the oxide, both requiring a preliminary operation, are employed; if the ore itself could be made into a pigment, that step would be eliminated resulting certainly in the cheapening of the product. This has not succeeded for white lead itself, but a pigment close to it has been made. Galena, natural lead sulfide (PbS), is roasted over a carbon fire. The coke is brought to incandescence and the powdered sulfide ore is thrown in at the top, at the same time admitting enough air for oxidation to the sulfate. The reaction is energetic. The product is

[1] "The Carter process of white lead manufacture," J. S. Staudt, Ind. Eng. Chem., 1, 758 (1909).

carried off by the fire gases, which are cooled and filtered (bags); it is a lead sulfate (PbSO$_4$ 75 per cent) and oxide (PbO 20 per cent) with some zinc oxide (ZnO 5 per cent), originating from the zinc ore (sphalerite) which occurs in the galenas used. The sulfate and oxide are present in a combined form; the pigment, which has been named sublimed white lead, is nonpoisonous, and is not decolorized by hydrogen sulfide; in these two respects it is superior to white lead.[2]

A process for making "super-sublimed white lead" has been perfected.[3] Molten lead is atomized by air under 40 pounds pressure, and natural gas under pressure of 15 pounds forced in at the outlet from the atomizer (see Fig. 172); a white flame forms, directed in a furnace. Sulfur dioxide is

FIGURE 172. — Lead atomizer-burner for super-sublimed white lead; *A*, gas supply; *B*, air; *L*, molten lead passage; *D*, dead spaces which help keep the lead liquid. (From Dr. Calbeck's article, by permission.)
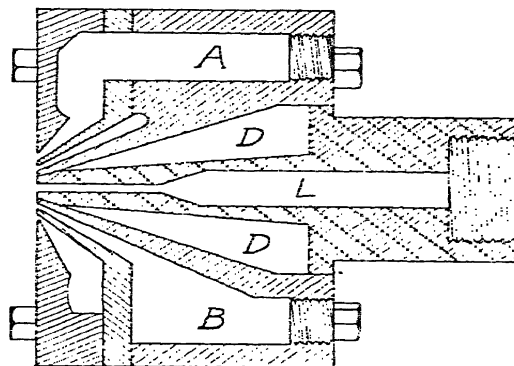
fed into the flame in the proper volume to produce a basic sulfate of the composition PbO.2PbSO$_4$. The dust passes through a cyclone dust box, cooling goosenecks, and is collected in a bag filter. The brightness of this pigment surpasses that of practically any other white pigment, while its whiteness is superior to that of any lead pigment and compares favorably with that of zinc oxide by the French process.

ZINC OXIDE

Zinc oxide is made in several ways. The original one, still in use, is the French or indirect process, in which zinc metal (spelter) is heated in stoneware retorts, the metal vaporized and burned in a combustion chamber placed at the mouth of the retort. An exhauster draws the white dust to an air chamber first, where the heavier, less desirable particles are deposited, then to a filter chamber, where the fine dust is collected.

In order to obtain the whitest pigment a very pure spelter must be used; if it contains lead for instance, a frequent impurity in zinc, the lead burns to litharge and gives a yellowish tinge, a serious fault. To

[2] John A. Schaeffer, *Scientific American Supplement*, Nov., 1912, p. 276.
[3] J. H. Calbeck, *Trans. Am. Inst. Chem. Eng.*, **14**, II, 13 (1924).

render the lead harmless, there has been developed a modified indirect method, in which the burning is done in air mixed with carbon dioxide; the lead is changed to white lead and thus the yellow tinge is avoided. The zinc oxide is unaffected. This modification has been extremely successful and has made possible the use of spelters containing appreciable quantities of lead.

Another modification is to use a retort open at both ends, and to send in at one end carbon monoxide which passes over the heated metal and assists in its vaporization. The two burn together as they issue from the other end of the retort into a combustion chamber; the resulting flame is an intense yellow-white. A simple sketch (Fig. 173) shows the disposition
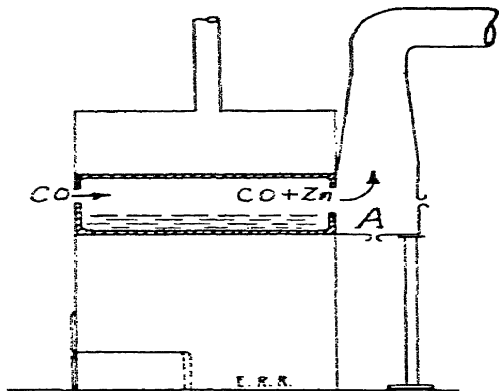
FIGURE 173.—Retort for vaporizing zinc in a stream of carbon monoxide; the two are burned together in the combustion chamber A, to manufacture zinc oxide.

of the apparatus. An exhauster pulls the fumes through a cooling chamber and forces them through bag filters.

A direct process, that is, one producing the oxide directly from the ore, was developed by Mr. Weatherill about 75 years ago for the New Jersey Zinc Company. In the Weatherill furnace, designed for this purpose, franklinite, an oxide of zinc containing also iron and manganese (Zn 18 per cent), mixed with coal is burned on a grate; the natural oxide is first reduced and then re-formed by the air and carbon dioxide from the fire. Provision is made to admit more air over the fire if there should rise unburned zinc vapors. The grate is a casting with tapering holes, not bars. The residue on the hearth is made into spiegeleisen, a manganese-iron containing also carbon.

It is feasible to use a low-grade carbonate ore (smithsonite) for the direct production of zinc oxide. In such a plant at Leadville, Colorado, 2000 pounds of ore are well mixed with 1100 pounds of coal and wetted to have 20 per cent moisture; this batch is shoveled onto the grate of a Weatherill furnace on which a coal fire is burning. Air is forced into the closed ash-pit; the temperature is 1000° C.; the burning requires 6 hours. The gases which pass out with the dust are cooled in a U-shaped 4-foot-diameter flue, 600 feet long. At the end of the trip, the gases are

140 C.; an exhauster sends them into cotton filter bags 20 feet high by 2 feet wide, which retain the dust, while the gases and water vapor pass out.[4]

Lithopone. Lithopone is formed when a solution of zinc sulfate is mixed with one of barium sulfide; barium sulfate and zinc sulfide are formed; they are both white. $ZnSO_4 + BaS = BaSO_4 + ZnS$. This precipitate is not suitable for a pigment, however, until it has been dried, heated to a high temperature in a muffle furnace, and plunged when still hot into cold water. Lithopone is 28 per cent zinc sulfide and 72 per cent barium sulfate, with slight variations; it has fair covering power, is brilliant white, and is cheap. It is extensively used in interior wall coatings.

Blanc fixe is precipitated barium sulfate. The original barium mineral may be the witherite, a carbonate, or the barite, the sulfate; if the latter, it is reduced by carbonaceous materials in a furnace, giving the sulfide. The sulfide is dissolved in water, the solution filtered, and treated with, for example, sulfuric acid, precipitating the sulfate; this is washed and dried. Blanc fixe is also a by-product in one of the hydrogen peroxide processes (Chapter 18).

The capacity and the covering power of blanc fixe are not high; it is prized chiefly because it is the most permanent white of the white pigments. It is used also as a filler in rubber goods, linoleum, etc., and as an indicator in X-ray treatment.

Antimony oxide Sb_2O_3 is another white pigment now available on the commercial scale; it is used in conjunction with titanium oxide, because it reduces the chalkiness of the latter pigment.

Titanium Oxide and Titanox. A newcomer in the field of white pigments is titanium oxide (TiO_2), which is very opaque and hence has a considerable hiding power. In addition to the oxide, a composite pigment is made which has met with much success; it consists of titanium oxide precipitated on calcium sulfate or barium sulfate and is called Titanox. Of the latter especially, thousands of tons a year are now marketed; this is still but a small percentage of the white lead and zinc oxide tonnage.

The chief ores are rutile (titanium dioxide, TiO_2) and ilmenite, the double oxide of iron and titanium; they occur in many localities, but only certain deposits are worked, among which are the sands in Florida and a deposit in Quebec. There are two ways to extract the ores in order to form the pure titanium dioxide: The ore may be heated in a reverberatory furnace with sodium sulfate and coal, the resulting melt lixiviated, and the solution boiled with dilute sulfuric acid; or the concentrated ore may be treated directly with sulfuric acid, decanting from undissolved matter, diluting, and boiling the dilute acid solution; the titanium dioxide precipitates.

In order to prepare the composite pigment with calcium sulfate, the procedure is as follows[5]: The concentrate is digested at 100° to 150° C. with 2.5 parts of 95 per cent sulfuric acid, and then transferred to a lead-

[4] *Met. Chem. Eng.*, **13**, 631 (1915).
[5] U. S. Patent 1,155,462.

lined vessel. On adding 3 volumes of water, the titanium sulfate dissolves. The exact equivalent amount of calcium chloride in solution is added, and calcium sulfate precipitates, suspended in the titanium solution. Digesting 5 hours at 100° C. causes the titanium to separate out gradually, coating the suspended sulfate, according to the reaction

$$Ti(SO_4)_2 + 2CaCl_2 + 2H_2O = TiO_2 + 2CaSO_4 + 4HCl.$$
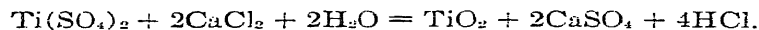
The precipitate is filtered, dried, and calcined; its content of titanium dioxide fluctuates from 20 to 25 per cent, of calcium sulfate from 80 to 75 per cent. The composite pigment with barium sulfate base is made in a similar way; to the solution of titanium sulfate, barium chloride or sulfide in solution is added; barium sulfate precipitates at once, and on that solid, during the two hours' subsequent boiling, the titanium oxide is deposited.[6]

Red Lead. Red lead is made from litharge, and litharge may be prepared in several ways. The oldest method, still practiced, is to heat lead metal in a low-arched reverberatory furnace [7] with the usual bridge wall dividing the fireplace from the hearth. The atmosphere is kept oxidizing by allowing much air to enter; the temperature is just above the melting point of lead oxide, PbO. As the oxide forms, it floats on the surface and is pushed to one side by iron hoes. When enough oxide has collected, it is drawn off by means of the hoes, cooled, ground, and levigated. The color is buff. A continuous furnace has been successful, in which air jets impinge on the surface of the lead so as to sweep the molten oxide to the front end of the oval furnace; fresh lead is added in a stream so regulated that the amount of lead in the furnace remains the same. The molten oxide overflows into a conical receiver; its content when cold is broken up, ground, and air-floated to remove unoxidized lead particles.

Litharge is also made as a by-product in the manufacture of sodium nitrite. Sodium nitrate is melted in a large iron pot, kept at 340° C. Lead in thin plates is added. After they have disappeared, the heat is maintained 20 minutes; the brown mass formed is then cooled and extracted with water, and sodium nitrite crystallized from the decanted solution. The residue is litharge; it is washed, and used for red lead or as it is.

Red lead is made by calcining litharge in a muffle furnace into the muffle of which a current of air is admitted. The temperature must be maintained within narrow limits, near 340° C. The period is usually 48 hours.[8]

Rouge, Fe_2O_3, is made on the large scale by roasting ferrous sulfate crystals, $FeSO_4 7H_2O$, from the pickling vats for steel; water and sulfur oxides are driven off and led through a tall stack to the atmosphere. The familiar red of barns and factory buildings is due to rouge. The shade can be varied considerably by altering the intensity of firing. It is very cheap. Its use for polishing glass is based on its freedom from grit.

[6] U. S. Patent 1,236,655.
[7] Chapter 4.
[8] "The lead and zinc pigments," C. D. Holley, New York, John Wiley & Sons, Inc., 1919.

Ultramarine is a blue; it is a double silicate of aluminum and sodium containing sulfur. Chrome yellow is lead chromate; prussian blue is the iron salt of ferrocyanide; the two mixed give a good green, but chrome green is usually made by co-precipitating chrome yellow and prussian blue. Antimony sulfide is yellow; manganese oxide a brown (bistre); basic copper acetate is green. Red lead is made by heating litharge as stated in the previous division; white lead carefully roasted gives a red-orange. Ochres are impure iron oxides, brown to red; they are mainly natural products, but artificial ochres are invading the field, and are finding favor because they are more uniform and no more expensive. Artificial cinnabar, made from mercury and sulfur, is a brilliant red. There are many other inorganic pigments, and they are mixed in every conceivable way. Organic dyes in the form of their insoluble salts with calcium and barium are used more and more, alone in some cases, admixed with the usual pigment to heighten the shade in other cases. They are chiefly mono-azo dyes.[9]

Carbon Black. "Carbon black, an extremely finely divided form of carbon (0.025 to 0.05 micron), is made by the impingement of the flame of natural gas upon moving metallic surfaces. It should be sharply distinguished from another important black pigment, lamp black, also a carbon pigment, but consisting of the free soot or smoke collected in chambers from burning hydrocarbon oils or hydrocarbon gases. The amount of air is limited, so that complete combustion such as would be insisted on under a boiler cannot take place.

"Lamp black is the older pigment; it has been made for thousands of years by the Chinese, Egyptians, and other ancient races for the manufacture of ink. Carbon black is a modern pigment.

"Carbon black is finer than lampblack, stronger in tinctorial power, blacker in color. In addition to displacing lamp black for inks, paints, and lacquers, carbon black has recently been found to improve enormously the durability of rubber goods; this explains why the rubber industry now takes over three-quarters of the carbon black production. In 1931, the amount produced was 265,000,000 pounds, the greater part in the Panhandle district, Texas. The production was (Bureau of the Census):

	1935 Pounds	Price per pound
Carbon black	352,749,000	4 cents
Bone black	31,847,653	3.96 "
Lamp black	3,581,429	9.3 "

"By suitable changes in the supply of secondary air, the size and change of tips, distance from, and speed of collecting surfaces, wide variations in color and in other properties of carbon black can be achieved.

"Recently new valuable properties of carbon black have been discovered, namely that it improves the insulating properties of rubber insulation and also the dielectric properties of insulating (transformer) oils. Carbon black is probably the most finely divided colloid available

[9] Chapter 28.

in unlimited quantities and at very low cost; for this reason there is every likelihood that it will find many new applications in the arts. It is a new material in the world's history and as such constitutes practically virgin territory for research."[20]

Lamp black is made from crude oil or fuel oil, by burning it with an insufficient amount of air and collecting the soot. Gas black is made similarly from natural gas; it has a deeper black, recalling velvet, and is more expensive. The white pigments have been discussed in detail; grays are made by adding a small amount of black with some green or brown to the white pigment.

PAINTS

A paint consists of a pigment, a vehicle, and a drier; it is applied to inside or outside surfaces, and in a day or so hardens to an unbroken film which prevents contact with rain, smoke, direct sunlight, and loss of moisture to the atmosphere; it is a preservative coating. On steel it prevents the rapid deterioration and destruction called rusting.

The vehicle is usually linseed oil, and this may contain the driers; such a prepared linseed oil is "boiled oil"; or, raw linseed oil may be used and the driers added when mixing.[11] Driers are usually the oxides, resinates, oleates or acetates of cobalt, manganese, lead, and occasionally zinc; they form compounds with the oil and accelerate the oxidation of the oil by the atmosphere. The oil itself does not actually dry; it hardens by chemical change, oxidation, accompanied, especially in the case of tung oil, with polymerization.

There are several requirements for a good pigment. It must be opaque, so that its hiding power may be high; the greater the hiding power, the less paint is required per square foot of surface. It must mix well with the oil. It must be inert to gas impurities in the atmosphere; inertness insures freedom from disintegration. Among other desirable properties it should not darken when exposed to hydrogen sulfide; preferably it should be non-poisonous. Finally its cost will determine the choice in many cases.

The pigments used for protection, hence for covering, primarily, are white lead, zinc oxide, lithopone, blanc fixe, Titanox, and rouge; to these, coloring substances are added in small quantities.

Paints are frequently mixed by hand with oil just before using; prepared paints are mixed by machinery; an example will be found under enamels.

VARNISHES AND ENAMELS

The materials for varnish making are certain vegetable oils, a resin, a small amount of drier, and a thinner. From the standpoint of the varnish maker, vegetable oils fall in three groups: the drying oils, the semi-drying oils, and the non-drying oils. Linseed oil is a drying oil;

[10] Based on private communication from Dr. W. B. Wiegand, Binney and Smith Company, N. Y., October, 1932.
[11] Raw linseed oil and boiled oil are discussed in Chapter 29.

when exposed to the air, it sets in about a day and a half. Soya bean oil is a semi-drying oil; it requires weeks to dry. Castor oil is a non-drying oil, after months it is still liquid. The drying and semi-drying oils are glycerol esters of unsaturated organic acids; they can take up oxygen and in doing so, harden, which is termed "drying." The non-drying oils are esters of saturated acids and cannot take up oxygen. Hence they do not dry.

The oils chiefly used in varnish making are linseed oil, chinawood oil also called tung oil, perilla oil, and soya bean oil (described in Chapter 29). Tung oil heated for 5 minutes to 550° F. (288° C.) cools to a solid gel, while linseed oil heated for several hours cools to a viscous liquid merely, indicating how sensitive to heat the former is.

Perilla oil comes from Manchuria; it dries to a harder film than linseed and about as fast. Soya bean oil has certain unusual properties: it can be bleached on heating, and it yellows less fast than any other oil, so that it is used in white enamels. A newcomer is oiticica oil, from Brazil, which is receiving much attention just now.

FIGURE 174.—A copper kettle on wheels for varnish making.
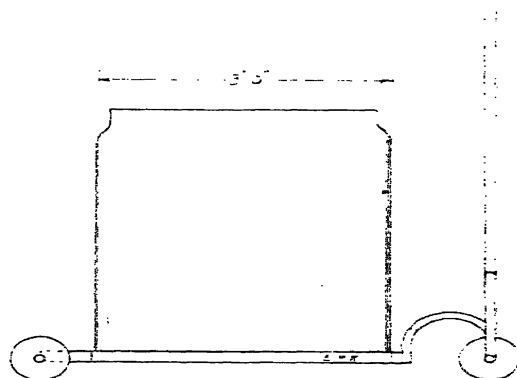
Natural resins are exudations formed on trees long since disappeared by decay; when they lie under a few feet of loose ground they are called fossil resins or copal. The hardest is the Congo copal; there is also a Manila copal, an East Indian and a New Zealand copal; the latter is called kauri. Amber is a variety of copal. To these must be added rosin and ester gum. Natural resins are frequently used in conjunction with synthetic resins, to modify their properties, and to lower their cost (thus rosin added to phenolic resins).

Synthetic resins have been introduced in varnish formulas in an effort to shorten the drying period; such formulas allow drying within four hours. There are two other points in favor of the inclusion of synthetic resins in varnish formulas; a larger percentage of resins may be incorporated, and these resins absorb ultra-violet light without alteration, protecting by their screening effect the more sensitive constituents. About half the varnishes are made with oil-soluble synthetic resins. The

manufacture of such "oil-soluble resins" is described in Chapter 35 on synthetic resins, in which synthetic resins for molding compounds, a distinct product, are also presented.

In order to hasten the drying of the varnish, driers are added. Lead, manganese and cobalt in the form of oxides are used, and the amount is small; for instance for cobalt, an amount of oxide equivalent to 0.1 per cent of cobalt is sufficient; for lead, 0.5 per cent must be used.

Thinners must be introduced so that the oil-resin coating may be applied in thin layers. Turpentine was largely used formerly; when its price reached one dollar a gallon, there was stimulated a search for other thinners, such as a heavy naphtha fraction from petroleum, and xylene and toluene, which may be obtained for around 16 cents a gallon. Turpentine is now much cheaper, 40 cents a gallon (1937). The naphtha solvents have proved superior solvents, however, and have come to stay; among other things they are particularly well suited to the alkyds and phenolic resins.

The relative proportions of oil and resin vary in the several kinds of varnishes. A high-resin varnish would contain to each 10 pounds of resin, 1 gallon of oil, $1\frac{1}{2}$ gallons of thinner, 0.4 per cent lead as lead soap. A long-oil varnish would have to each 2 pounds of resin, 1 gallon of oil, $1\frac{1}{2}$ gallons of thinner and 0.5 per cent lead as lead soap. A better classification of varnishes is as follows:

"Short"—12-15 gal. oil/100 lbs. resin................ for furniture to be rubbed
"Moderately short"—15-25 gal. oil/100 lbs. resin..... for many household enamels
"Medium length"—25-35 gal. oil/100 lbs. resin....... for spar and floor varnish
"Long oil"—35-50 gal. oil/100 lbs. resin............. for durable exterior varnishes

In making a "high-gum" varnish, 100 to 200 pounds of resin are placed in a copper kettle on wheels, and this is pushed over the flame of an oil burner set below the floor. The temperature is raised rapidly to 600° F. (315° C.). Blown linseed oil [12] is now added, and the two together are heated long enough to give a uniform liquid. The driers are next added in powder form and stirred in; then the kettle is pulled off the fire and cooled in the room. When fairly cool the thinner is added, after which the varnish is forced through a plate-and-frame press which retains any suspended material. The clear filtrate is pumped into storage tanks and aged for a period of several months. Numerous laboratory tests on color, clarity, viscosity, specific gravity, drying power on glass, water-proofness and toughness of film, are run.

An *enamel* is a varnish containing a pigment. It is made by mixing a pigment with thickened linseed oil in a ball mill preferably, followed by further mixing with a varnish in a mixing tank with paddle. The roll mill is also used extensively for pigment mixing, instead of ball mills. The older buhrstone mill is used only for pigments of hardness greater than that of the steel rolls. For whites, white lead, lithopone, titanox, or blanc fixe, are employed.

[12] Chapter 29.

The roll mill of the older type has three rolls which rotate at different speeds, so that there is a rubbing action which causes unmixed oil droplets to be torn open and brought in contact with the pigment.   The rolls are hollow, and water cooled.   The three-roll mill is losing its place in the manufacture of enamels and paints, to the five-roll mill, whose rolls rotate much faster, and whose capacity is three times that of the three-roll mill with the same sized rolls.

Baking japans are varnishes made up with asphaltum instead of resin; the baking is done, for metal surfaces, at 400° F. (204° C.) and lasts 3 to 4 hours.   This temperature melts the asphaltum easily, and distributes it evenly; during the baking the oxidation of the oil is rapid, so that on removal of the article the coat is dry.   A very beautiful black luster is obtained; black automobile fenders are coated in this way.   By baking at lower temperatures, varnishes containing the usual resins may be used.

A spirit varnish contains alcohol or similar solvent, and dries by the evaporation of the solvent; it contains shellac,[12a] as a rule, or certain other resins such as mastic, sandarac and dammar.   Several new synthetic resin finishes are coming into wide use which might be included under the term "spirit varnish," since they dry by evaporation of the solvent; they are: vinyloid, dissolved in ketones; pliolite, in hydrocarbons; tornesit, a chlorinated rubber hydrocarbon, in toluene and xylene.

Spar varnish contains Chinawood oil and ester gum, and is waterproof.

LACQUERS

A lacquer is a protective coating which dries by evaporation of volatiles, and whose essential film-forming constituent is a cellulose ester, nitrate, acetate, or other.   The liquid lacquer applied to the surface to be protected contains, for example: (1) nitrocellulose or nitrated cotton, called "cotton" for short in the trade; (2) the solvent, usually a mixture of two or more substances; (3) the plasticizer which remains in the film and keeps it softer; (4) the diluent; (5) a dye or pigment. Table 63 shows the ultimate particle size of the various pigments used.

A lacquer coating dries rapidly, by the evaporation of the solvents; the standard varnish dries slowly, partly by evaporation, partly by oxidation.

Nitrocellulose, also called pyroxylin, is made by nitrating cotton linters with mixed acid.   The nitration is not allowed to proceed as far as when making nitrocellulose for explosives, for the highly nitrated cellulose (12.5 per cent N and over) is not soluble in the selected solvents; for that reason, a "cotton" containing only 11 to 12.4 per cent N is prepared.

TABLE 63.—*Ultimate Particle Size of Various Standard Pigments.*

Materials	Maximum residue on No. 325 screen (opening 44 microns) (Per cent)	Average ultimate particle size (Microns)	
Carbon black	1.0	0.1	
Fine particle Zinc Oxide ("Kadox")	..	0.12 to 0.18	
Zinc oxide (Florence French process "Green Seal")	1.0	0.21 to 0.26	
Lithopone	1.0	0.25* to 0.35	
Titanium barium pigment	1.5	...†	...
Zinc sulfide	..	...†	...
High strength lithopone	..	...†	...
American process zinc oxide	1.0	0.28	0.35
Lampblack	1.0	0.4	
High leaded zinc oxide	1.0	0.35	0.45
Iron oxide (Spanish)	3.0	0.4	0.6
Low leaded oxide (5% leaded)	1.0	0.50	0.65
Sublimed white lead	1.0	0.65	0.67
Basic carbonate white lead (Old Dutch Process)	1.0	0.75	1.21
Chrome green	2.5	...	...
Ultramarine blue	..	5.0	

* According to H. Green secondary particles (aggregates) of lithopone may be composed of from 2 to 50 ultimate particles. When dispersed the individual particles vary in size from colloids to particles perhaps a half a micron in diameter.

† No definite figures available but approximately the same as lithopone. Table from "Pigments in nitrocellulose lacquer enamels," H. A. Nelson and W. C. Norris, *New Jersey Zinc Co. Research Bull.*, September (1927).

The linters are purified from oils by boiling with caustic, washed, and if colorless lacquer is sought, bleached. The nitration is carried out by placing 32 pounds of cotton in 1500 pounds of mixed acid; the great excess of acid is taken to insure negligible change in concentration over the period of nitration due to consumption of nitric acid and production of water.

$$C_{24}H_{40}O_{20} + 8HNO_3 = C_{24}H_{32}O_{12}(NO_3)_8 + 8H_2O$$
cellulose   *nitrated cellulose*
or nitrocellulose

The reaction given here is an idealized one and is meant to indicate the change taking place: a single nitrocellulose is really not formed, but a series of them, with various numbers of nitrate groups in the molecules. The total nitrogen content is the guide.

After 15 minutes in the acid, the cotton is dropped to a centrifuge below, to remove the adhering acid. It is then beaten in pulping machines (8 hours), boiled in poaching tubs (12 hours) with several changes of weakly alkaline waters. Finally the 25 per cent adsorbed moisture is displaced by denatured alcohol forced in under a pressure of 300 pounds. At this stage the nitrocellulose moist with alcohol resembles cotton waste in appearance; it is made in a few plants, and is bought by the varnish maker who dissolves it and blends it to suit.

Originally the nitrocellulose so made was dissolved in amyl acetate for example, and articles dipped in the solution. On evaporation of the solvent, a film remained. It was soon observed that only 6 ounces of

nitrocellulose could be dissolved in one gallon of the solvent; more gave a solution too viscous to flow. In fact, with 6 ounces, the resulting solution was quite thick. Nitrocellulose which gives rise to such solutions is called *high viscosity nitrocellulose.* It became desirable to modify the nitrocellulose so that a greater amount of it might be placed in solution, and yet have a solution thin enough to be applicable with a spray gun. Such a modified material is *low viscosity nitrocellulose,* the manufacture of which is detailed in this division. It is now possible to place 24 ounces of nitrocellulose with 16 ounces additional gums in one gallon of solvent, hence 40 ounces in all of film-forming material, instead of only 6. The important product now is low viscosity nitrocellulose. The gums which are suitable additions are dammar, shellac, kauri, rosin ester, and similar ones.

High viscosity "cotton" is still made, for use in bronzing liquid, and in many lacquer formulas, because the film made from low viscosity cotton is weaker than the one made from high viscosity cotton.

Continuous Digester for Low Viscosity Nitrocellulose

Nitrocellulose of low viscosity is produced by heating the first product of nitration with water under pressure. This was done at first in batch digesters, of small size, then of gradually increasing size as the control of the action was improved. Finally, batch digesters of welded steel, brick-lined, capable of handling a batch of 4000 pounds of nitrocellulose with 60,000 pounds of water, were put in successful operation. As the viscosity drops (that is, the viscosity of the solutions of the treated nitrocellulose) during the heating, there is a decrease in the nitrogen content, from 12.25 to 12.05, and at the same time gas forms. In large units of the batch type, the venting of the gas formed during the action presents some difficulties. For that reason, and in order to realize the incident economies, a further improvement was sought in the form of a continuous operation.

In the method devised [13] the suspension of the nitrated cotton (1 part), still in the fibrous form, in water (20 parts), is pumped continuously through a tube 1000 feet long, curled back and forth in several tiers, and 4 inches wide, by means of motor-driven centrifugal pumps connected in series. The charge travels constantly and after 25 minutes emerges and rises into a standpipe 200 feet high, from which it overflows to receiving tubs below. Any bubble formed in the heating tube is carried along so that no gas pockets form. The tube is heated by a steam jacket [to 132° C. (270° F.) for example] for a distance from the entrance to the tube, then it is insulated for most of the rest of the way, except that near the end it is cooled by a water jacket. An acid-resisting alloy is used. The rate of flow and the temperature are controlled; by keeping them constant, the desired reduction in viscosity is maintained.

The excess water is removed in centrifugals, leaving the product moist,

[13] "Nitrocellulose of low viscosity," M. G. Milliken, *Ind. Eng. Chem.,* **22,** 326 (1930).

or it is displaced by alcohol in a dehydrating press, leaving the nitrocellulose alcohol-moist. A test solution is prepared as described below.

Low viscosity nitrocellulose may also be produced by heating the product of nitration with benzene or ethyl alcohol.[14]

The viscosity depends upon the treatment of the nitrocellulose, as has been stated, but it also depends to some extent upon the solvent. The viscosity of the liquid lacquer can be increased by adding nonsolvents such as benzene; it can be reduced by adding such "true solvents" as acetone or ethyl acetate.

The method used for testing viscosities of lacquers is the falling ball method. A steel ball $\frac{5}{16}$ inch in diameter and weighing 2.043 grams is made to fall through 10 inches exactly in a glass tube 14 inches high, 1 inch in diameter, with the liquid tested at 25° C. (77° F.). The time required for the fall is taken with a stop watch. The concentration of the "cotton" to be tested, and the nature of the solvent must be specified. The specifications suggested by the Hercules Powder Company have been generally accepted: 16 ounces of "cotton" on the dry basis, and as solvent the formula known as No. 366, consisting of ethyl acetate 20, ethyl alcohol 25, toluene 55 parts, all by weight. With the relation given, a solution of a little over 12 per cent nitrocellulose results. In terms of such a solution and of the falling ball test, a high viscosity nitrocellulose will be 200 seconds for the fall, while low viscosity cellulose will be one-half second. Intermediate viscosities are provided.

Plasticizers. By itself, the film of nitrocellulose left, after the solvents evaporate, contracts, so that it wrinkles and buckles away from the surface being coated. This serious defect is successfully counteracted by using in the formula a substance which will not volatilize when the film dries, hence will remain in the film, and which renders it plastic. Such substances are castor oil, camphor, diethylphthalate, dibutylphthalate, diamylphthalate, tricresyl phosphate, tributyl phosphate, butyl stearate, and many others. Castor oil is used if pigments are to be incorporated in the lacquer.

By adding certain substances such as the chlorinated diphenyls, the Aroclors, there is secured a decrease in the flammability of the film, in addition to a plasticization.

Solvents for Lacquer. The first solvent for nitrocellulose was mixed alcohol and ether; this gave collodion or "new skin." It was improved by the addition of a little castor oil, giving now "flexible collodion." For the protective coating, the early solvents were amyl acetate, butyl acetate, ethyl acetate, the latter two of which are now the most frequently used. The newer solvents are glycol derivatives (Chapter 25), amyl propionate, butyl lactate, cyclohexanol acetate, and many others.

The boiling points of some of the more important solvents are listed below:

[14] U. S. Patents 1,553,494-5.

Solvent	B. pt.	
	° C.	° F.
Ethyl acetate	77	170
Butyl acetate	125	257
Amyl acetate	137	278.6
Cyclohexanol acetate	170	338
Cellosolve (Glycol mono ethyl ether)	134	273.2

A differentiation between the several solvents is well made in two ways; by the vapor pressure at room temperature,[15] and by the rate of evaporation.[16]

On drying, too volatile a solvent cools the film considerably, so that atmospheric moisture condenses on it; this is called blushing. The remedy is to use a higher boiling, hence slower evaporating solvent.

Pyroxylin (the mixed nitrocellulose molecules resulting on moderately nitrating cellulose) placed in a solvent and apparently dissolved, gives merely a colloidal solution, not a true solution. A good solvent is one which takes up a large quantity of nitrocellulose, and still remains fairly fluid; a non-solvent takes up none at all. A diluent is a non-solvent which is miscible with the solvent; it is added in amounts insufficient to cause a precipitation of the nitrocellulose. Toluene, benzene, and petroleum naphthas are diluents.

Cellulose Acetate Lacquer. Cellulose acetate (Chapter 22) as the main film-forming material in the lacquer formula has the great advantage that it is not flammable. Two factors, however, have retarded its wider spread, one is that, for a given weight of film-forming material, the viscosity of a solution of acetate is not as low as one of nitrocellulose; the other is the higher cost. The plasticizer is generally tricresyl phosphate.

Uses for Lacquer. There are three main outlets for lacquer which require a tremendous tonnage. First, artificial leather, which is made by coating a cotton fabric with a pyroxylin solution and then embossed to simulate the grain of a leather. Second, the finish for automobile bodies; a nitrocellulose or pyroxylin finish is superior to the standard gum-linseed oil varnish finish in durability, resistance to abrasion, cracking, chalking, and in rapidity and ease of application; it is inferior to varnish in luster. The somewhat duller but more durable pyroxylin finish is now very popular. Third, interior decoration, woodwork, furniture and the like; here lacquer has the advantage over paint that it dries in less time.

The application is mainly by a spray gun; within a few hours the coating is dry. One coating suffices. Brushing lacquers are also prepared, and marketed.

Production figures for pigments, paints, varnishes and lacquers are given in Table 64.

[15] Graph on p. 673, *Ind. Eng. Chem.*, 17 (1926).
[16] Graph on p. 500, *Ind. Eng. Chem.*, 20 (1928).

TABLE 64.—*Selected Items Indicating the United States Production of Pigments, Paints, Varnishes and Lacquers in 1935.*[*]

			Price per pound
Dry pigments			
White lead (basic carbonate and sulfate)	pounds	116,794,732	5 cents
Zinc oxide	"	257,203,951	4.95 "
Lithopone	"	322,639,266	4.44 "
Iron oxides (natural, synthetic)	"	112,423,238	2.75 "
Whiting	"	125,351,666	.66 "
Chrome yellows and oranges	"	39,170,554	9.5 "
Iron blues (Prussian blue)	"	5,582,836	35 "
Chrome greens	"	7,959,753	20.8 "
Ready-mixed paints	gallons	89,449,713	144.8 "
White lead in oil, pure	pounds	169,629,876	7.62 "
Varnishes, synthetic-oleoresinous	gallons	14,539,204	1.16 dollars
Varnishes, resinous, except synthetic	"	15,839,553	.97 "
Nitrocellulose lacquer, clear	gallons	9,332,624	1.38 "
Nitrocellulose lacquer, pigmented	"	11,760,134	2.10 "
Thinners for lacquers	"	18,591,545	.69 "
Enamels (oil, ester gum, natural resin)	"	20,422,809	1.61 "
Enamels (synthetic resin type)	"	11,039,339	2.00 "
Bleached shellac	pounds	12,524,732	19.4 cents
Spirit varnish	gallons	7,908,191	1.01 dollar

[*] Bureau of the Census.

PRINTING INK OR NEWS INK

Printing ink should not be compared to ordinary writing ink; in that sense it is not an ink at all, but rather a paint. It must dry as fast as applied, mainly through penetration of the paper. It is made by mixing carbon black or lamp black with linseed and rosin oils, rosin varnish and a drier.

Rosin oil is used in part, because it is cheaper than linseed oil. It is made by distilling rosin in simple stills, fired by the staves from the rosin barrels; there passes over water, acetic acid, an impure "pinoline," then rosin oil; the residue is pitch and is run off hot. The rosin oil is refined by a second distillation. Rosin varnish is made by heating rosin till water, acetic acid, and pinoline have passed over, then running all the residual liquid into a mixer containing warm linseed oil. This linseed oil is previously hardened by the following treatment: It is heated in a kettle over an oil burner and when hot enough, flashed, that is, ignited; it is allowed to burn in this way for four hours, then the flame is extinguished by placing a cover over the kettle. Only 5 per cent of the oil is consumed during the burning.

The proper proportions of rosin oil, rosin varnish, and lamp black are mixed in a preliminary way, then this mixture is fed to a number of rather small mills consisting of two horizontal steel disks, of which the upper one rotates on its hollow shaft, and drags the lower one, which is larger, with it but in constantly changing relation. The mixture is fed in from a gallon pail above, through the hollow shaft. The discharge is at the edge by a scraper.

Colored inks for printing are made similarly, using as pigments the

metallic compounds of organic dyes as well as inorganic pigments such as prussian blue and chrome yellow. Some of the organic pigments are lithol red, lake Bordeaux, helio fast red.[17]

The importance of news ink is indicated in the statement that the New York Tribune alone consumes over 4,000,000 pounds of such ink in a year.

OTHER PATENTS

U. S. Patent 2,033,916, organic phosphates, to impregnate wood, and as plasticizers; 1,848,660, process for the manufacture of a red pigment; 1,981,210, manufacture of a green mineral pigment consisting of cobalt chromite and magnesium orthotitanate; 1,846,188-7, production of white pigments from titanium dioxide; 1,833,087, enamel containing barium and strontium compounds; enamel consisting of white lead, zinc oxide, barium fluoride, chinawood oil, linseed oil, turpentine, gum manila (gal. ethyl alcohol and acetic ether; 1,753,616, application of lacquers to metallic surfaces; 1,801,340, nitrocellulose lacquers, and 1,884,255, same, with resins of the coumarone and indene types (see Chapter 35); 1,756,100, colored nitrocellulose varnishes; 1,756,267, non-penetrating varnishes and lacquers from reactive resins of the phenol-aldehyde type; 1,817,183, manufacture of lithopone; 1,821,441, paint and enamel with a granulated or powdered base, that can be applied in stippled form; 1,891,679, manufacture of varnish and paint oils, using mixtures of reduced hydrocarbon polymers with varying amounts of drying oils; 1,865,191, a lacquer containing cellulose nitrate, an artificial cyclic ketone resin and a solvent containing at least 20 per cent propylene glycol diethyl ether; 1,826,667-8, piperidine and anisidine as plasticizer in cellulose acetate combinations, tri-m-oxyphenyl phosphate as plasticizer and fireproofing agent with cellulose acetate; 1,870,556 (trichloracetamide), 1,836,701 (trimethylene glycol dibutyrate) for similar purposes; 1,836,687, for coating fabrics to form leather substitute; 1,833,136, for making a sheet material of good flatness of hydrolyzed cellulose acetate.

PROBLEMS

1. One ton of lead in the form of buckles is made into white lead having the composition (idealized) $2PbCO_3 \cdot Pb(OH)_2$. If the yield is 95 per cent, how many pounds of white lead will be obtained?

2. With pure materials, what would be the weight of barium sulfate in 1 ton of lithopone?

3. A rouge which analyzes 92 per cent Fe_2O_3, the rest water, is made by heating 5000 pounds of copperas. How much rouge is obtained?

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[17] "The manufacture of organic dyestuffs," André Wahl, translated from the French by F. W. Atack, London, G. Bell and Sons, 1914, p. 115; *also* "Printing inks," W. F. Harrison, *J. Chem. Ed.*, **3**, 408 (1926).

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"Cellosolve and its derivatives in nitrocellulose lacquers," E. W. Reid and H. E. Hofmann, *Ind. Eng. Chem.*, 20, 497 (1928), with many formulas for every kind of lacquer.

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It has been said that the amount of soap consumed in a country is a reliable measure of that country's civilization. There was a time when soap was a luxury; it is now a necessity. The vast amounts of soap now manufactured in every civilized country are possible only because through chemical science new raw materials have become available; the tallows and animal greases of the old days are supplemented by coconut, palm, cottonseed, and other oils.

Chapter 32
Soap and Glycerin

Soap is the sodium or potassium salt of stearic and other fatty acids; it is soluble in water, and this solution has cleansing properties which are unequaled. Other substances cleanse, but soap is the only one which does so without injury to skin or fabric. Other metals also form compounds with fatty acids, thus calcium, aluminum, and lead; but these compounds are insoluble, and serve as lubricants,[1] in paints, and for other purposes; they are always designated as "calcium soap," "lead soap."

Soap is made by the action of a warm caustic solution on tallows, greases, and fatty oils, with the simultaneous formation of glycerin which at one time was wasted, or left in the soap, as it still is in certain cases; glycerin has become a valuable by-product.[2] The reaction[3] is as follows:

$$3NaOH + (C_{17}H_{35}COO)_3C_3H_5 = 3C_{17}H_{35}COONa + C_3H_5(OH)_3$$

| *caustic soda* | *a typical fat, glycero-stearate or glyceryl stearate* | *sodium stearate (soap)* | *glycerin* |
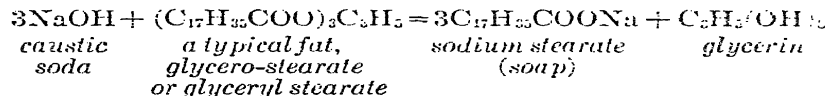
It may also be made by the action of caustic soda on the fatty acid, when no glycerin is produced:

$$NaOH + C_{17}H_{35}COOH = C_{17}H_{35}COONa + H_2O$$

| *caustic soda* | *stearic acid* | *soap* |
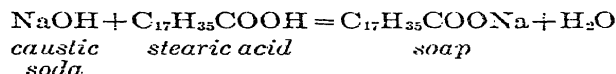
The glyceride used is never a single one, but a mixture of several, so that the soap produced partakes of the properties of each. Sodium stearate dissolves too slowly; while the sodium soap made from coconut oil dissolves too fast; a mixture of the two has the right solubility. The reaction is generally performed in steel vats, in which a solution of caustic soda is mixed with the fat or oil, and heated; the soap is in solution in the water and must be separated by the addition of salt (NaCl). For high-grade soap, a steel tank with the upper part stainless steel, is used. The glycerin remains in the water and is drawn off at the bottom. The raw materials then are caustic soda or caustic potash (KOH), fats, greases and fatty oils, and salt.

[1] Chapter 24. Ordinary soap, that is sodium soap, is also an important lubricant.
[2] 8 to 10c a pound.
[3] *Compare* the reaction given in Chapter 29.

RAW MATERIALS

The caustic soda is usually received in drums of 700 pounds of solid caustic, and this is made into a strong solution by inverting the opened drum over a steam jet with provision to collect the solution formed. The caustic may also be crushed and dissolved with occasional stirring. Soap plants situated near the alkali factory receive the caustic in form of a 50 or 25 per cent solution; for long distances this more convenient strength would mean a high freight bill. The caustic may also be made at the plant by causticizing soda ash with lime; this is rarely done at present. Caustic potash is usually received as the solid, in drums.

Beef and mutton tallow of all grades are used, from the best No. 1 edible grade to the cheapest grade recovered from garbage; the grades chosen depend upon the quality of the soap to be made. Tallow is not used without admixture with other fats or oils, for it gives a soap which is too hard and too insoluble; it is usually mixed with coconut oil.

TABLE 64a.—*Materials Consumed in Soap Making in the United States for 1935 (Bureau of the Census, Department of Commerce).*

	Pounds
Tallow, inedible	663,002,000
Grease	98,000,000
Coconut oil	229,711,000
Olive oil foots	31,507,000
Palm kernel oil	37,173,000
Palm oil	87,311,000
Fish oils	109,970,000
Marine animal oils	28,440,000
Olive oil inedible	1,090,000
Cottonseed oil	1,857,000
Corn oil	2,828,000
Soybean oil	2,549,000

Coconut oil is a solid (m. pt. 20° to 25° C.); it gives a soap which is fairly hard, but too soluble by itself. It is the basis of marine soaps, as it lathers even in salt water. According to the country of origin and to the manner of isolation, coconut oils differ in their content of free fatty acids; the lower the fatty acids, the better the quality of the oil; this applies to all fatty oils. Of the coconut oils, Cochin oil is the highest grade.

Palm oil is usually colored orange to brown, and has 60 per cent free fatty acids, hence does not give much glycerin; it is an important raw material, and is used for toilet soaps. Palm oil may be bleached by warming it and blowing air through it. Palm kernel oil is an oil of light color. Castor oil is used for transparent soap.

Olive oil of the lower grades, no longer edible, is much favored by the soap maker; for fine toilet soaps olive oil of the edible grade is used, but it is denatured by the addition of oil of rosemary, so that its import duty is low. Castile soap is a sodium-olive-oil soap, and also the Savon de Marseille.

In the refining of cottonseed oil a treatment with a solution of caustic is the first step (Chapter 29); the alkaline liquors contain the foots and are used in soap making. Cottonseed oil itself is also used, usually combined with foots, or after being treated to form the free acids (Twitchell process).
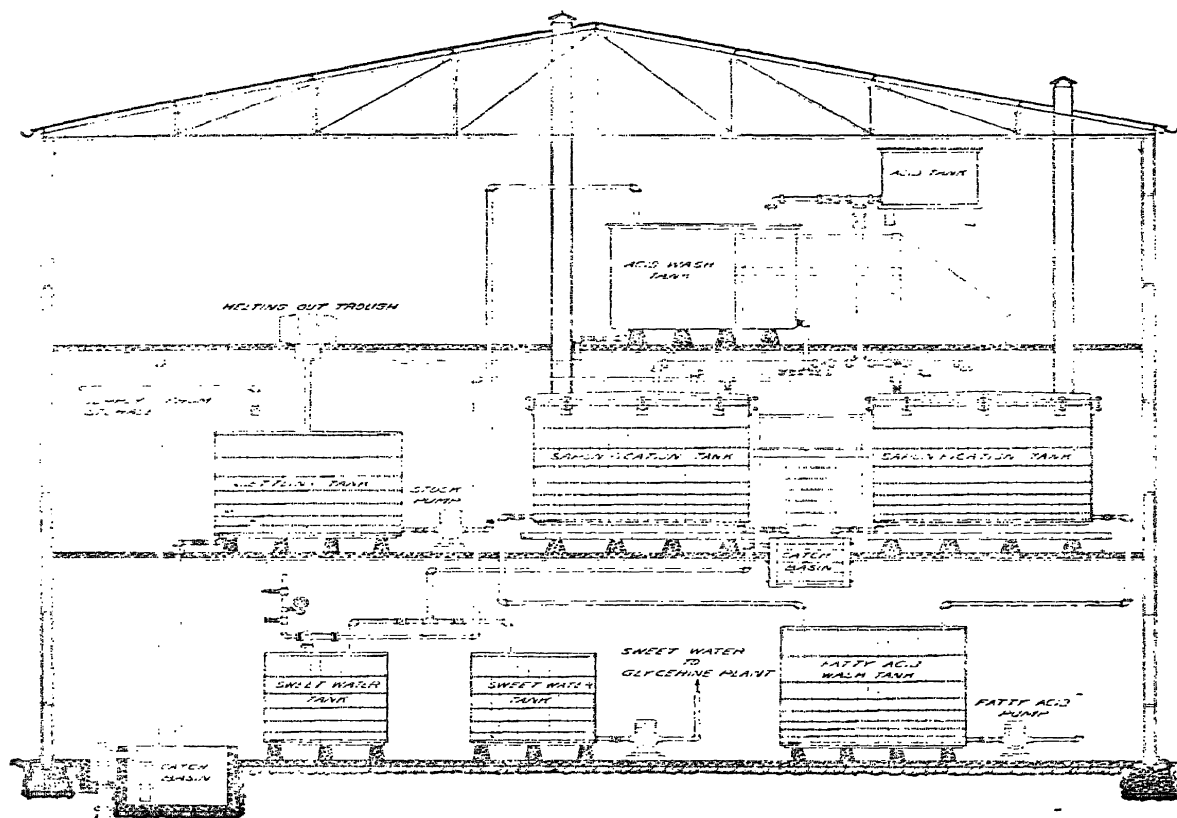
FIGURE 175.—Twitchell process fat-splitting plant. with settling tank. two saponification tanks, sweet water tanks, and fatty acid wash tank. (Courtesy of Wurster and Sanger, Inc.. Chicago.)

The word grease to the buyer of soap stock means an animal fat, softer than tallow, obtained by rendering diseased animals, or from house and municipal garbage, from bones,[4] and tankage. Sales in 1935 of "grease including soap stock" were 306,116,512 pounds, at 5.9 cents a pound; while "tallow, inedible," also a soap stock, was 431,976,463 pounds, at 6.3 cents a pound. Rosin serves for laundry soap, and is discussed under that heading.

Free Fatty Acids. Instead of the glycerides, the free fatty acids may be used; these are produced in a preliminary operation, the best

[4] Chapter 36.

known of which is the Twitchell process.[5] (*See* Fig. 175.) In this process, any quality of oil or grease is changed into slightly colored free fatty acids; the glycerin is recovered from the acid liquor, and in addition a residue of the distillation of the crude fatty acids called candle tar. The process consists of heating the foots or grease with 30 per cent sulfuric acid in the presence of a small amount (0.5 per cent) of naphthalene sulfonic acid as a catalyst; the boiling is done in open, lead-lined wooden tanks. The melted fatty acids produced, insoluble in water, are freed from acid by water addition; the sulfuric acid waters contain the glycerin; by adding lime the sulfuric acid is precipitated as calcium sulfate, filter pressed, and from the filtrate the glycerin recovered by concentration. The fatty acids are agitated with water to remove any sulfuric acid, and used as such, or they may be distilled under very low pressure (10 to 20 mm. Hg); the still is heated by open fire. (*See* Fig. 176.) The distillate is white at first, and yellow for the whole[6]; the
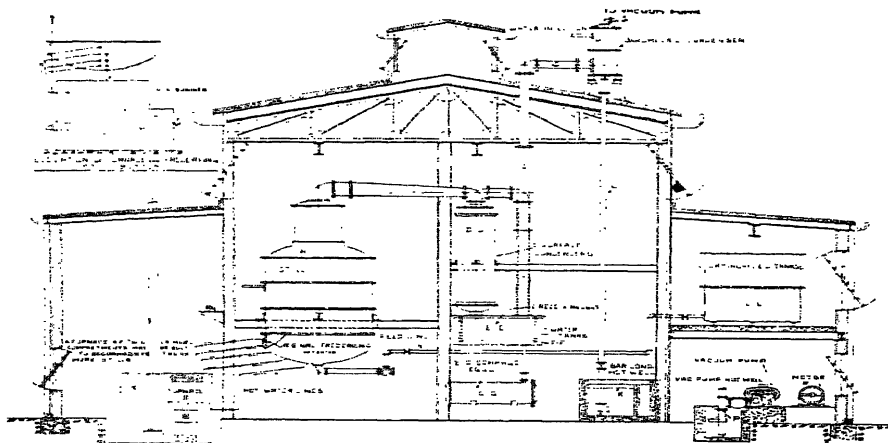
FIGURE 176.—Fatty acid distillation plant. (Courtesy of Wurster and Sanger, Inc., Chicago.)

residue in the still, the candle tar (or stearin pitch), is used for prepared roofings. Stearic acid produced by this process is an excellent material for making candles; it is a white solid, melting at 69° C.,[7] and is an article of commerce.

The advantages claimed for the Twitchell and similar processes are: The concentration of the glycerin is higher in the filtrate from calcium sulfate than in the glycerin water in the boil process, and it is free of salt. The fatty acids may be made into soap by means of soda ash:

[5] O. T. Joslin, *Ind. Eng. Chem.*, 1, 654 (1909); also "Thomssen's soap-making manual," New York, D. Van Nostrand Co., 1922.

[6] New catalysts which cause less or no darkening have come into use replacing the naphthalene sulfonic acid; the Pfeilring, and the Kontact; *see* p. 117, "Thomssen's soap-making manual," New York, D. Van Nostrand Co., 1922. The yellow color is a drawback. The Twitchell process proper does not include the distillation.

[7] The commercial stearic acid melts at 65° C. or lower.

the more expensive caustic is not necessary. There is a decrease in the odor of strong-smelling stocks.

MANUFACTURE OF SOAP

Ordinary toilet soaps and laundry soaps are made by the "boiled process", which is adapted to batches ranging from 1000 pounds to 800,000 pounds; a second process, the "cold process," is used for special soaps.

By the boiled process, a batch of 300.000 pounds of soap for example would be made in a steel kettle 28 feet in diameter and 33 feet deep, with a slightly conical bottom. A solution of caustic soda testing 18° to 20° Bé. (12.6 to 14.4 per cent NaOH) is run into the kettle, and the melted fats, greases, or oils pumped [8] in next. The amount of caustic is so adjusted that there is just sufficient to combine with all the fatty acids liberated. Heat is supplied by direct steam entering through a perforated coil laid on the bottom of the kettle. There is no stirrer but agitation is provided by a direct steam jet entering at the base of a central pipe (compare illustration). The kettle is kept boiling until saponification is complete, which requires about 4 hours; salt (NaCl) is now shoveled in, allowed to dissolve, and the boiling continued until the soap has separated, forming the upper layer. The lower layer contains glycerin and salt, and is drawn off at the bottom of the kettle; its concentration is described under glycerin. The whole operation just described is termed the *saponification change* and requires about 8 hours.

The salt used is chiefly rock salt; it is recovered in large part, and used over again.

On the second day, water is run in and boiled with the soap; any glycerin caught in the soap is dissolved, and the solution, a lower layer again, is run off at the bottom; it is combined with the first glycerin water.

On the third day, a 10° Bé. fresh lye (6.5 per cent NaOH) is run into the kettle and boiled with the soap. Any glyceride which escaped the first treatment is saponified; any uncombined free acid is neutralized. The soap, which is not soluble in the alkaline liquor, acquires a grainy structure. This is called the *strengthening change*. After settling, the lye is run off and used in a new batch.

On the fourth day, the soap is boiled with water, which is chiefly incorporated in the soap. By this treatment the melted soap acquires a smooth, glossy appearance. On settling, three layers are formed: the upper layer, the melted soap; the middle layer, the nigre, which consists of a mechanical mixture of soap in a soap solution; a very small lower layer containing some alkali. The melted soap is pumped away by means of a swing pipe without removing the nigre; the latter may remain in the tank and be worked into the next batch; the small lower layer is wasted. This operation is the *finishing change,* and lasts several days because the

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[8] A Taber pump is suitable; see Chapter 41.

settling must be very thorough. For the whole cycle of operations, about one week is customary.

The melted soap is pumped to driers, crutchers, or storing frames; it contains 30 to 35 per cent water. One pound of fat or grease makes about 1.4 pounds of kettle soap; the factor varies with different raw materials.

Laundry Soap. The procedure for laundry soap by the boiled process is the same as has just been described, but the raw materials are, for example, 4 parts tallow and greases and 2 to 3 parts rosin. The
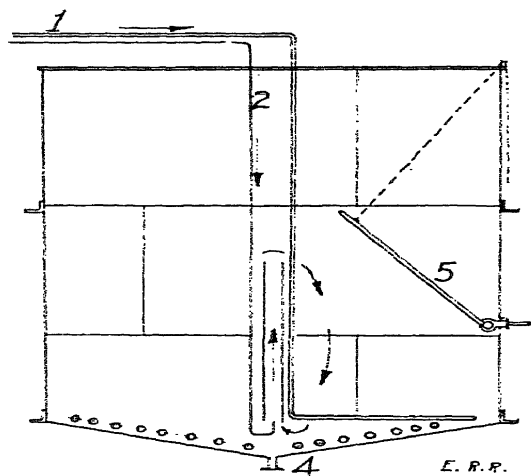
Figure 177.—Kettle for soap by the boiled process: 1. steam inlet for the perforated steam coil; 2. steam for agitation; 4. run-off for lye liquors and glycerin liquors; the soap is pumped out through the swing pipe 5.
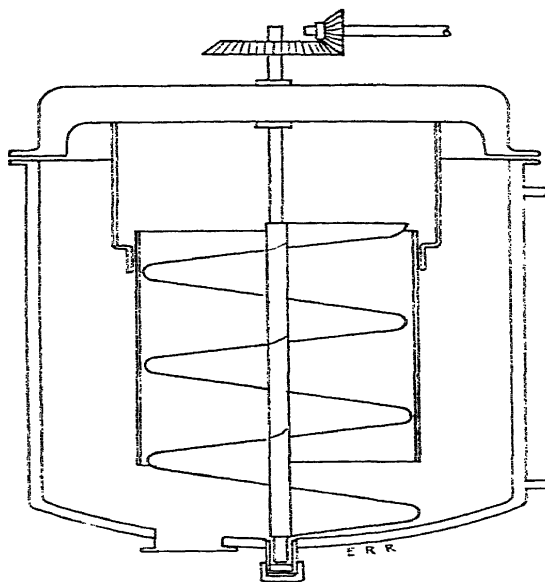
Figure 178.—The soap crutcher.

latter is added after the greases have been saponified, and it is added in the form of sodium resinate; this is made in a separate kettle, by the action of soda ash (which costs less than caustic) on the rosin. A saponification does not take place with rosin, which consists of abietic acid chiefly, and not glycerides; the formation of the sodium resinate is rather a neutralization. Rosin is cheaper [9] than grease, and gives a rather soluble soap.

The kettle soap for laundry is pumped from the kettle to a crutcher, which is a smaller tank (Fig. 178) fitted with a special agitator and with a steam jacket, and one of the following materials is added: silicate of soda, 41° Bé. (with 40 per cent solids), up to 30 per cent; soda ash, 2 to 5 per cent, either alone or with borax, 1 per cent; or trisodium phosphate, up to 5 per cent. The mixture is crutched until homogeneous; it

[9] Normally $10 to $14 for a unit of 280 pounds; while tallow and greases average 6 or 8c a pound.

is then run off at the bottom of the crutcher into a "frame," a box 4 feet high, 5 feet long, and 15 inches wide, with removable sides, two of metal and two of wood; the base is a small truck. The content of such a frame, of which there are hundreds, is 1000 to 1200 pounds of soap. A crutcher 4½ feet high and 3½ feet circular diameter has a capacity slightly greater than that of one frame. The content of the frame hardens in 3 days to a solid block, and the sides of the box may then be removed. The block is dried somewhat, then cut into slabs, and these into bars and pieces. The water content of the finished soap is about 30 per cent.

Milled Toilet Soap. For a milled toilet soap, the kettle soap is shredded, partly dried, mixed with essential oils, milled in stone mills, pleaded, that is, pressed into bars, and these cut into cakes. A milled toilet soap contains about 15 per cent water.
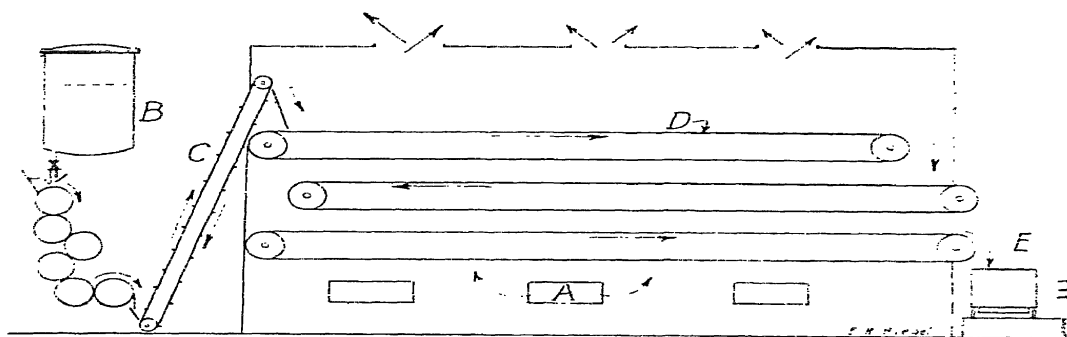
FIGURE 179.—An American soap shredder and drier. The melted soap from insulated tank *B* is fed to the chilled rolls, reaching the knife where the ribbons are formed; they are elevated by *C* to the wire screen *D*, passing to the other two and discharging at *E*; the warm air enters at *A*, and leaves at the top.

The kettle soap [10] is pumped directly into the operating tank of a French or American soap drier (Fig. 179) and from there fed gradually to a series of steel rollers, chilled by ice-cold water. The film hardens and passes six rolls, each rotating a little faster than the preceding one. The last roller is fitted with a knife with saw-tooth edge, which tears the soap into ribbons one-half inch wide. These are elevated by a broad endless belt with wooden cross pieces to the uppermost of three horizontal endless wire belts. The shreds drop from the first wire belt to the second, then to the third, which delivers them, warm, to a receiving box on wheels. The wire belts are enclosed in a wooden closet, and warm air is forced through them, reducing the moisture of the ribbons from 30 to 15 per cent. They are next fed to a Ruchman mill, consisting of 8 granite rollers. The ribbons are sprayed with the essential oil chosen, as they enter the mixer; in the passage between the rolls,

[10] The soap is conveniently stored in the form of solid blocks made in the special box described under laundry soap as a frame; when needed, the blocks are cut in slabs, and these remelted in a special kettle.

which again move at increasing speeds, they are pressed together and mixed thoroughly. On leaving the last roll, a serrated knife cuts the newly formed sheet into ribbons again. These are still warm, and have the proper moisture content so that when fed to the next machine, the plodder, they coalesce perfectly on being forced by a spiral screw through a die; the screw and die are steam heated. A bar is obtained which can be cut into cakes by the movement of a frame with taut steel wires. Each cake is then pressed in a die to receive the trade mark and its final shape.

Cold Process Soap. In order to make soap by the cold process, a vertical crutcher such as described under laundry soap and shown in the illustration (Fig. 178) may be used (capacity 1200 pounds) or a horizon-
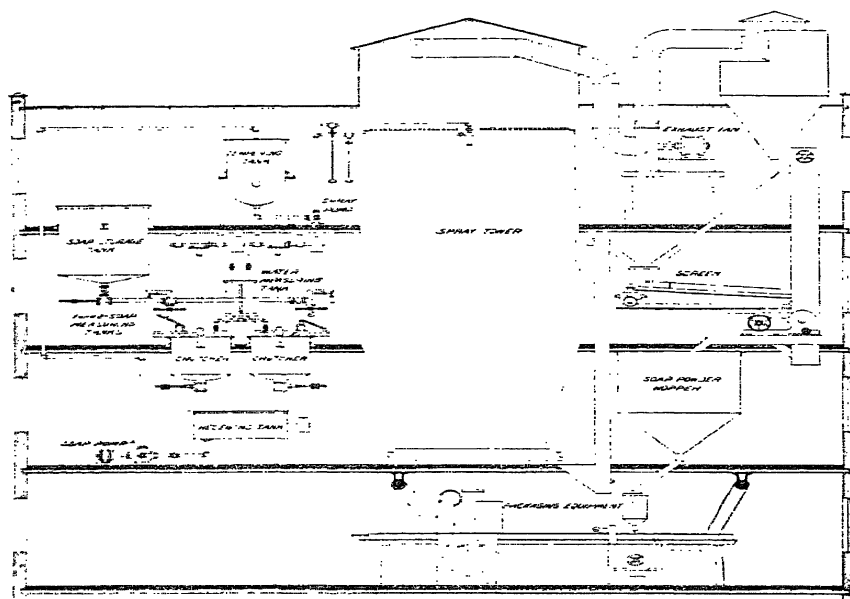
FIGURE 180.—Wurster and Sanger spray-process soap powder plant. (By permission.)

tal one of greater capacity. The fat is run in and heated to 130° F. (54° C.) by the steam in the jacket; then the lye is added and the mass agitated. The reaction is exothermic, so that the heat may be turned off at this point. After crutching for about an hour, the mixture stands for $3\frac{1}{2}$ hours; then it is agitated again, and rested again. The glycerin liberated remains in the soap, which is run off at the base of the crutcher into frames and milled as described under milled toilet soap; or the perfume may be added in the crutcher and mixed with the mass there, at the end of the operation.

Sodium and potassium soaps mixed are always made by the cold process. Potassium soaps are soft soaps; the potassium soap cannot be

salted out by NaCl, for the sodium soap forms; neither can it be salted out by potassium chloride, KCl. The process is used for shaving soaps, toilet soaps, and special soaps; certain laundry soaps are also made by this method. Shaving soap is a potassium-sodium soap containing free stearic acid in order to give the lather a lasting property.

Miscellaneous Soaps. Transparent soap is made in a variety of ways. One method requires the best coconut oil, castor oil, and tallow, which are treated with caustic soda lye by the cold process; the glycerin remains, and cane sugar and alcohol are added.

"Soap powder" is a hydrated mixture of soap 20 per cent, soda ash 40 per cent, and the remainder water. Powdered soap is very dry soap which has been reduced to a fine powder; it is used in dispensers in washrooms. Liquid soap is usually a potash soap dissolved in water, containing from 8 to 30 per cent; the solutions of 30 per cent and higher contain alcohol. The manufacture of soap powder may be illustrated by means of the spray tower system, shown in Figure 180.

The soap solution, containing, for example, 20 per cent soap and 40 per cent sodium carbonate, is sprayed into the tower through a special nozzle. As the small drops travel downward, they cool, partly by losing sensible heat to the air current which sweeps upward, partly by evaporation of water. The sodium carbonate crystallizes to $Na_2CO_3 . 10H_2O$, sal soda, thus binding the greater part of the water; only a small amount need be lost by evaporation to produce a dry powder.[11]

Textile soap is another specialty soap; it is made from olive oil and is run into barrels so that the buyer receives a cake the size of the barrel, and can cut it into slabs and bars to suit his requirements. Textile soaps for wool, silk, or cotton differ and formulas suitable for each are recommended.[12]

TABLE 65.—*Selected Items in the Soap Industry for 1935 (Bureau of the Census).*

	Pounds	Cents/Pound
Toilet soap	362,901,569	14.6
Laundry soap	420,519,270	4.75
Powdered soap	502,122,591	9.03
Soap chips, flakes, packaged	307,274,876	8.35
Soap chips, flakes, bulk	151,659,892	7.1
Washing powders	132,681,612	4.2
Scouring powders	186,494,781	3.12
Textile soap, including potash and foots soap	67,521,396	7.65

OTHER PROCESSES FOR SOAPMAKING

The lime soap process, used in Europe, has been tried by at least two firms in the United States; by one of these, its use has been discontinued. In this process, the fats are saponified by lime instead of caustic; the insoluble lime soap forms and separates without requiring salt addition. The glycerin liquor is therefore free from salt and its concentration much

[11] U. S. Patents 1,732,454 and 1,740,759.
[12] "Thomssen's soap-making manual," New York, D. Van Nostrand Co., 1922.

simplified. The lime soap is changed to sodium soap by treatment with soda ash.

Another process used chiefly in Europe is the autoclave process, which, like the lime process, is designed to produce a purer glycerin than is yielded by the boiled soap process. The fats and oils are saponified in a closed vessel, under pressure, when a fifth of the calculated amount of lime, or lime and magnesia, are sufficient for the hydrolysis of the glycerides, with the formation of the free acids, glycerin, and a moderate amount of calcium or magnesium soaps. The latter and the free fatty acids separate as solids, from which the glycerin water may be decanted or filter-pressed; this glycerin is almost pure.

GLYCERIN

Crude Glycerin. The spent lye drawn from the kettle in the boiled process contains the glycerin (5 per cent), the salt (10 per cent), some albuminous substances, free alkali, and soap in solution. The alkali content is normally 0.4 per cent or less; for purification, aluminum sulfate is added; there are formed aluminum hydroxide and aluminum soaps, both
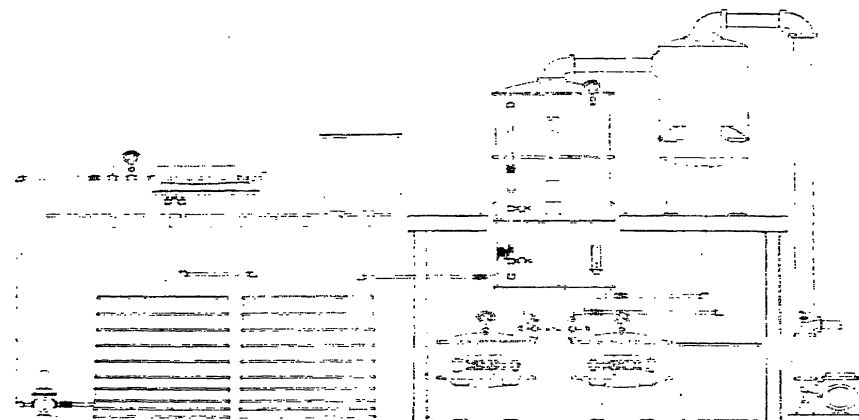
FIGURE 181.—A spent soap lye-treating plant (left) and a single effect vacuum evaporator for glycerin recovery, with the two salt boxes underneath. (Courtesy of Wurster and Sanger, Inc., Chicago.)

insoluble. This precipitate settles well in the slightly acid solution; it is filter-pressed, and the filtrate made slightly alkaline before concentration. (*See* Fig. 181.) The concentration is performed in a closed, upright cylindrical steel vessel with conical bottom, and fitted with a set of steam coils. The steam in the coils is low-pressure, 5 to 25 pounds; this is sufficient because the pressure on the liquid is reduced by a vacuum pump to well below atmospheric. Water vapor passes out, and when the specific gravity of the liquid has reached 29° Bé., the salt can no longer be held in solution, and separates, dropping into the cone. The whole content

of the evaporator is dropped into a steel box at the outlet from the conical bottom; in this salt box, the salt settles out. The supernatant liquor is sucked into the still; glycerin water from the soap kettle is run onto the salt, this suspension settled again and the liquor also sucked into the still. The salt, now fairly free from glycerin, is placed on a nutsch [13] filter and dried; it still retains 1 per cent of glycerin or so, but this is not lost, for the salt is used over again in the kettle room.

The liquid drawn back into the still from the salt box is much lower in specific gravity, for it has lost the salt; its glycerin content is about 49 per cent. The evaporation is continued until 80 per cent is reached, and the red liquid then obtained is the crude glycerin of commerce. The test for this stage consists of heating a small sample in an open dish, when a boiling point of 158° to 160° C. must be reached.

Crude glycerin is an article of commerce. It is the raw material of the glycerin distillers, a separate enterprise. Many of the larger soap-makers, however, distill the glycerin in their own plants.

Distillation of Glycerin. The crude glycerin with a red color is made into a purer, straw-colored glycerin by distilling it under reduced pressure, in a current of steam. The still is heated by a steam coil in which 110-pound superheated steam circulates; the pressure is made as low as possible, about 1 inch mercury,[14] or 25 mm. There comes over first the water contained in the crude, with some glycerin; after this is over, the steam jet allowing wet steam to enter the liquid is turned on and the glycerin comes over with the steam. The vapors pass through five air-cooled receivers in which the glycerin, with a little water, condenses, but which cannot hold the bulk of the water vapors; these pass on to a multi-tubed cold-water condenser with considerable surface where it is condensed rapidly. The condensed water, containing some glycerin, is termed sweet water; its amount is rather considerable, for about 3 pounds of steam are sent through for each pound of glycerin. The sweet water is evaporated to the strength of crude glycerin, and treated in the same way.

The glycerin gathered from the air-cooled receivers has a concentration of 85 per cent. By far the greater quantity is made into dynamite glycerin, by concentrating it again at reduced pressure, pulling away the water vapors until the content of glycerin is 99.8 to 99.9 per cent, and the specific gravity 1.262 at 15° C. Dynamite glycerin is straw-colored.

There is left in the still a residue, the foots, which contain the sodium sulfate formed by the aluminum sulfate treatment, glycerin, and organic impurities. The foots are treated to recover the glycerin content.

The distilled glycerin is made into the U.S.P.[15] grade by treating it while lukewarm with bone char, filtering, and redistilling the filtrate in a separate still used for nothing else. The distillate is treated with bone

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[13] Chapter 42.

[14] This means absolute pressure; the usual statement is 28 inches vacuum; if the normal atmospheric pressure at that locality is 29 inches, it is the same as 1 inch pressure absolute. The normal barometric pressure at sea level is 29.92 inches Hg.

[15] United States Pharmacopœia, *see* Chapter 30.

char a second time, filtered, and is then as white as distilled water. It has a strength of about 98 per cent, and a specific gravity of 1.258 at 15° C.

The yield of glycerin as dynamite glycerin or U.S.P. glycerin is about 90 per cent of the glycerin contained in the solution from the soap kettle.

A process for the manufacture of glycerin by the fermentation of sugar or molasses has been put into large scale practice. A yeast is used, and the fermentation is made to proceed in an alkaline medium by the addition of sodium sulfite, sodium phosphate, sodium carbonate, or any one of several other salts. Sugars which are suitable are grape sugar, glucose, fructose, inverted saccharose, treated starch. One kilo of sugar to which have been added 500 grams of sodium sulfite anhydrous, and 250 grams of magnesium sulfate, in 8 liters of water, with 100 grams of yeast, yielded in the best trial 13 per cent ethyl alcohol and 33 per cent glycerin.[16] An improved yeast which will bring about the fermentation of sugar to glycerin in half the normal time has been described.[17]

Glycerin is used for dynamite manufacture, in paper making, in the manufacture of rayon, cellophane, and in certain inks. It finds use in hydraulic brakes for automobiles, and in certain shock absorbers. The U.S.P. grade is used in the pharmacy, for lotions. Glycerin is valuable also as a solvent; as an anti-freezing mixture in automobile radiators it has found use in the past, but the synthetic ethylene glycol has displaced it to some extent.

In 1935 there were produced 24,041,800 pounds of crude glycerin, valued at 9.83 cents a pound, and 121,261,514 pounds of refined glycerin, valued at 10.7 cents a pound.

OTHER PATENTS

1,852,820, manufacture of a stabilized soap containing phenylphenolate; 1,853,807, on manufacture of resinous soaps; 1,887,743, transparent or opaque toilet soaps and medicated soaps; 1,874,388, rapid, continuous process and apparatus for making soap, intended to replace the cold process; 1,885,166, distillation of glycerin by injecting superheated steam; 1,837,010, production of pure glycerin.

PROBLEMS

1. A soap powder is to be made from a soap solution containing 20 per cent soap and 40 per cent sodium carbonate. Let all of the sodium carbonate be transformed into crystals of the decahydrate, and let the soap retain 5 per cent moisture. How much water will have to be lost by evaporation in order to reach apparent dryness of the powder?

2. Let the saponification reaction take place as stated in the introduction to the chapter, in the first reaction, with a fat. If 1200 pounds of NaOH (100 per cent) are consumed, how many pounds of glycerin are produced? If the caustic is in the form of 18° Bé. solution with 12.6 per cent NaOH, and the kettle has three times the capacity of the caustic solution, what would be the necessary size in cubic feet? Select dimensions which will reflect the shape of kettle shown in the illustration.

[16] U. S. Patent 1,511,734.
[17] U. S. Patent 1,551,997.

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"Effect of p_H on action of soap," F. H. Rhodes and C. H. Bascom, *Ind. Eng. Chem.*, 23, 778 (1931).

"Modern stearic acid plant," T. R. Olive, *Chem. Met. Eng.*, 36, 721 (1929).

Ever since the birth of modern chemistry, which is usually dated from the days of Antoine Louis Lavoisier, late in the 18th century, the men practicing the new science have controlled the manufacture of explosives: Lavoisier himself was the manager of the powder works of the French Government just before the revolution of 1789.

Chapter 33

Explosives

Explosives serve two main purposes. In times of peace, they serve as a labor-saving device in dislodging rocks, coal, and other minerals; in times of war emergency, they serve for the national defense against an enemy. As to the latter use, the day is undoubtedly approaching when all disputes will be settled on their merits, by court or council. It is proper in the meantime for every nation to provide the necessary explosives for the protection of persons, property, and institutions within its borders. When the day of universal peace arrives, explosives will continue to be manufactured, for as man's servant in the discharge of physical tasks, they have become indispensable. As an example of the advantages which explosives confer, the following may be given: It took 30,000 men 11 years to build a 3-mile tunnel for a Roman aqueduct; the same construction by means of modern machinery and high explosives requires only 100 men working 10 months.

TABLE 66.—*Uses of More Important Explosives.*

Dynamites (nitroglycerin with wood meal, nitrates, or kieselguhr)	high explosive for peace use
Blasting gelatin (nitroglycerin 90% and nitrocellulose 10%)	high explosive for peace use
TNT (trinitrotoluene)	high explosive for war use
Picric acid	high explosive for war use
Ammonium nitrate	high explosive for war use
Smokeless powder (nitrated cellulose gelatinized by acetone, in grains or sticks)	mild explosive for war use
Black powder	mild explosive for peace use
Mercury fulminate	auxiliary explosive, war use
Lead azide	auxiliary explosive, war use

An explosive is a chemical substance or a mixture of substances which, struck with a hammer or touched by a flame or electric spark, is suddenly rearranged with the formation of gases and the development at the same time of heat. If this rearrangement takes place inside a closed chamber, its walls are shattered. The substances which serve as useful explosives are comparatively inert, for they must be manufactured, handled, and transported without premature explosion. The extremely sensitive substances such as nitrogen tri-iodide, which explode at the touch of a feather, have no value as commercial explosives. Among the useful explosives a distinction is made between high explosives and ordinary explosives. The distinction is not on the basis of sensitivity, but on the basis of shat-

...ing power; nitroglycerin is a very sensitive high explosive; picric acid, an insensitive one. Very sensitive substances such as mercury fulminate and lead azide are used as primers, that is, to start the explosion of a less-sensitive substance, which a light blow would not set off. A list of the more important explosives is given in Table 66.

The uses listed in Table 66 are not exclusive in every case; thus dynamite is used in war to damage bridges and railroad tracks, in order to hamper a pursuing enemy. Smokeless powder is used in the small amount of peace-time ammunition consumed by hunters. Black powder is used in some types of military shells.

There are other substances which are of importance in the explosive industry for various purposes. Diphenyl amine is a stabilizer for smokeless powder; urea, similarly. Dynamite may contain anti-freezing agents.

<div align="center">PROPERTIES AND TESTS</div>

The shattering power, also called the brisance, of an explosive depends upon two properties, the strength of the detonation, and the velocity of propagation of the explosion within the explosive itself. The strength depends upon the volume of gases developed, and upon the amount of heat liberated. It is measured by performing the explosion of a known weight

FIGURE 182.—Dautriche test for velocity of detonation: 1, main fuse; 2 and 3, detecting fuses. The distance *E-S* is measured.
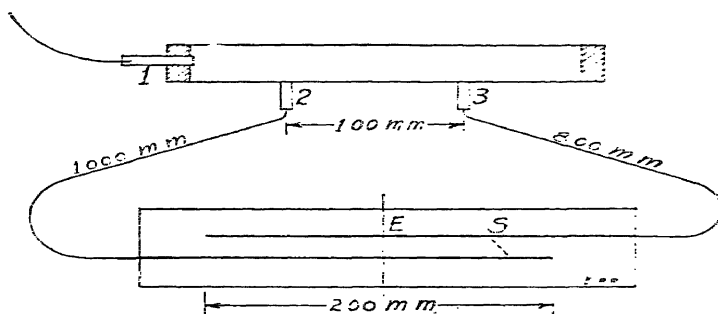
of the substance within the cavity of a lead block; the cavity is distended by the action. The volume of the distended cavity is a measure of the strength of the explosion (Trauzl test). Another method is the ballistic gun, a 500-pound mortar suspended as a pendulum, which shoots a 36-pound shot; the recoil of the mortar is measured. The two methods give concordant results.

The velocity of detonation or explosion is determined by the method of Dautriche. A tube filled with the sample is fitted with two auxiliary detonators, which are set off when the explosion passes them; each is connected to a standard trinitrotoluene fuse (copper pipe) which terminates at a thick sheet of lead $(3'' \times 15'' \times \frac{1}{4}'')$, as indicated in Figure 182. Each fuse on burning causes a bend in the sheet; the position of the point where the two bends meet relative to *E* is the measure of

the velocity.[1] Some values for strength and velocity of explosion are given in Table 67.[2]

The velocity of detonation depends upon the chemical constitution mainly, but very appreciably upon the density of the explosive, raised by compression; the denser, the higher is the velocity; thus for picric acid, it may be raised from 5000 to 7000 meters per second.

TABLE 67.—*Strength and Velocity of Explosion.*

	Strength by Ballistic Gun	Velocity in Meters per Second
Nitroglycerin	14.0	....
Ammonium nitrate 80%, TNT 20%	12.1	5920
Tetryl, tetranitromethylaniline[3]	12.1	....
Nitrocellulose, 13.35–13.50% N	12.0	6383 (d. 1.25)
Picric acid	10.6	8183 (d. 1.55)
Ammonium nitrate	10.5	....
TNT trinitrotoluene, the standard	10	7600
Dynamite, 50% nitroglycerin	9.8	....
Black powder	..	300 (d. 1.04)

The sensitiveness of explosives is measured by dropping a weight from different heights; the greater the height required to cause explosion, the less sensitive is the substance. The stability on storage is determined by observing time and temperature required to evolve fumes of nitrogen tetroxide (NO_2), and in other ways. Of great importance is the uniformity of a commercial brand, so that results may be calculated beforehand, and exactly duplicated by using the same weight of the same material.

Explosives intended for use in coal mines in which there is fire-damp (methane, CH_4) present, which forms explosive mixtures with air, are tested by firing them in a long gallery resembling a smoke stack laid on its side, in which the conditions in the mine are reproduced. Those which fail to explode the gas mixtures are placed on the permissible list of the Bureau of Mines.[4] Such explosives have short flames of short duration; their velocity of detonation is about 3000 meters per second.[4] Their detonation temperature is reduced by a proper choice of ingredients, and particularly by the addition of water in the form of crystal water of admixed materials; such temperature reduction does not materially affect their strength.

In general the duration of the flame is inversely proportional to the temperature of detonation. Secondary flames, due to evolved gases which are combustible (CO), are repressed by the addition of alkaline salts.

---

[1] "Explosives, their history, manufacture, properties and tests," A. Marshall, Philadelphia, P. Blakiston's Sons & Co., 2d ed., 1932.

[2] From "Strength and velocity of detonation of various military explosives," W. C. Cope, *Ind. Eng. Chem.*, 12, 870 (1920), and from p. 307, "High explosives," by Colver, London, Crosby Lockwood & Sons, 1918.

[3] Tetryl is

$$O_2N \underset{NO_2}{\overset{NO_2}{\diamondsuit}} N(CH_3) . NO_2$$
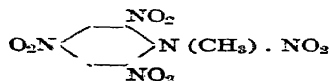
[4] "Permissible explosives, mining equipment, and apparatus approved prior to January 1, 1923," S. P. Howell, *Bur. Mines, Tech. Paper No. 333.*

Duration and length of flame are studied by photography. The following values will indicate the time and size: gunpowder (black), duration 0.077 second, length 110 mm. (for 100 grams); gun-cotton (nitrocellulose mixture) 0.0013 second, 97 mm. (for the same weight). Ammonium nitrate and picric acid show much shorter flames.

The pressure developed by the explosion of a nitrocellulose mixture in a gun chamber is about 3 tons per square inch.

EXPLOSIVES FOR WAR

The military explosives for artillery fall into two classes: the propellant, which fills the cartridge and serves to force out the shell with a high velocity, and the bursting charge, carried by the shell, which shatters it after it has traveled a definite distance. For rifles, the cartridge contains the propellant, which drives out the solid steel bullet. The hand grenade has no propellant; it contains only a bursting charge; it is propelled by hand.

The propelling charge is a mild explosive; its velocity of detonation is relatively low; its function is to exert a sustained pressure on the shell, forcing it to take the rifling [5] of the gun bore, and continuing in effective pressure until the shell is free from the gun. Nitrocellulose in fiber form is a high explosive, but gelatinized, so that its surface is greatly reduced, it becomes a mild explosive. Its rate of burning is regulated further by the shape, diameter, length, and perforations of the sticks into which it is formed; it is the propellant generally used, with or without certain admixtures. For a 3-inch (diameter) shell, the cartridge is about 1 foot high, of cold-drawn brass; the shell also is about 1 foot over all. In order to fire the propelling charge, a hammer blow ignites a small fulminate cap forming part of the primer, which contains a sizable amount of black powder; this explodes in turn, and flashes into the propellant. The primer is 1 inch in diameter, and is threaded into the thick base of the cartridge. The shell is crimped into the cartridge, surmounting it, and the two form one piece which, after being filled at the arsenal, is moved about as a unit.[6]

The shell may contain only the high explosive, such as TNT, or TNT mixed with ammonium nitrate (Amatol), or picric acid or its salts; its only function is to travel to the desired point and there be shattered into fast-moving fragments which become the actual missiles. The shell may contain, besides the bursting charge, somewhat reduced, balls packed in rosin or black powder; it is then a shrapnel shell.[7] Finally it may contain instead of the balls, a war gas.[8] The shell is ignited by a fuse whose

[5] The rifling of the gun consists of grooves; the shell has a band of copper which is wider than the body of the shell; the soft copper is forced into the wide grooves and "takes" the rifling; the grooves are curves, and as the shell progresses, it acquires a rotational motion which permits a wider and truer trajectory.

[6] During 1915, the unfilled 3-inch shell and cartridge sold to a foreign government for $14; while the war was in progress the cost of smokeless powder to the government was dropped from 53 cents a pound to 44 cents.

[7] Named after Lieutenant Shrapnel, the inventor.

[8] Chapter 34.

length is adjusted by the relative lengths of a horizontal fuse in a ring which may be turned a part or all [9] of a circle, to a canal leading the flame to a black powder charge which in turn flashes the high explosive; the first fuse is ignited automatically as the shell emerges from the gun. The shell is steel, with a heavy base and often an aluminum nose piece.

NITROCELLULOSE

The introduction of nitrocellulose as a military explosive became possible only through the labor of the British scientist, Abel, who showed that complete removal of impurities would permit the production of a material with reproducible properties, and relatively safe to handle.

Cotton waste is cleaned by hand, and carded to a fluffy open mass; this is dried by warm air, and the cotton is then cooled in closed boxes, to prevent reabsorption of moisture (the moisture content is 1 per cent or less). The nitration was formerly performed in pound lots, in earthenware pots, for a period of 24 hours after a preliminary 3-minute dip; the product was then centrifuged and washed. The nitration is now performed in the centrifugals themselves, so that no transfer is needed in order to free the nitrated cotton from the excess acid. Still another way is the direct displacement method, in which the acid after action is displaced by cold water floated on quietly through a rubber hose, while the spent acid is drawn off at a corresponding rate from the base of the pan. The water forms a separate layer; as more is passed in, the cotton loses adhering acid.

The composition of the mixed acid for the nitration is not far from the following figures: 71 per cent H_2SO_4, 21 per cent HNO_3, 7.5 per cent H_2O, and 0.5 per cent HNO_2 impurity.

In the displacement method, 20 pounds of cotton per pan are nitrated with 650 pounds of mixed acid, which is more than is used in the older pot method, but the time is shorter, $2\frac{1}{2}$ hours against 24 hours. The nitrated cotton is next boiled with several changes of water for 10 periods, which vary from 12 hours (the first) to 2 hours, the last; this boiling with water replaces the previous practice of using a dilute caustic solution. The boiling is followed by shredding and reduction to short lengths of fiber in a beater engine, as used in paper plants.[10] After draining, the wet pulp is best pressed into short rods which are dried in a warm closet. Until shredded in the beater, the cotton retains its original appearance; it is somewhat harder, and, unlike the original material, it is soluble in potassium hydroxide solution.

The standard military powder in the United States requires a nitrocellulose which contains 12.8 per cent nitrogen on analysis, which agrees with the formula $C_{24}H_{30}O_{10}(NO_3)_{10}$; the equation is

[9] The length of the horizontal, adjustable fuse controls the time of burning before explosion hence the distance the shell travels before it bursts. Instead of a time fuse, some shells have percussion caps, set off as the shell strikes an obstacle.

[10] Chapter 21.

$$C_{24}H_{40}O_{20} + 10HNO_3 = C_{24}H_{30}O_{10}(NO_2)_{10} + 10H_2O$$
cellulose *nitrated cellulose*
or nitrocellulose

The water formed is bound by the sulfuric acid present and does not hinder the reaction.[11]

In the preparation of the smokeless powder (U. S.), the nitrocellulose is mixed with alcohol in the first step; another procedure is to treat the pressed wet pulp from the beaters with several changes of alcohol, thus avoiding the drying operation. Ether is next incorporated in a mixing machine with water-cooled jacket; a small addition of diphenyl amine takes place also, as a stabilizer. The proportions are: 84 pounds nitrocotton, 26.4 pounds alcohol, 3.6 of water, 48.4 of ether, and 0.38 of diphenyl amine.[12] The soft mass is sieved free from coarse grains, and forced through a die into rods of various diameters, which are made into lengths, as desired, by an automatic cutter. The brown, clear jelly-like mass so obtained is freed from the solvents, ether and alcohol, in drying-rooms with fans. The recovery of the solvent vapors diluted with air is not always undertaken.

Cordite [13] is another nitrocellulose powder, which consists in its modified form (Cordite M. D.) of nitrocellulose 65 pounds, nitroglycerin 30 pounds, mineral jelly (soft paraffin) 0.5 pound. The gelatinizing agent is acetone, which may be recovered from the drying-room vapors by absorption in sodium bisulfite. There are many other smokeless powders with nitrocellulose as base, with modified formulas, used by the various nations. Nitrocellulose itself generates on explosion carbon monoxide in addition to other gases [14]; by the addition of an oxidizer such as potassium nitrate, the poisonous and combustible carbon monoxide is changed to harmless carbon dioxide.

Nitrocellulose is used for other purposes than explosives; the degree of nitration is less, just sufficient to render the cellulose soluble in ether, for example. Cotton is not always chosen for these lower nitrated materials; it is often replaced by wood pulp.[15]

PICRIC ACID AND TNT

Picric acid, symmetrical trinitrophenol. $1\text{-}OH\text{-}2,4,6\text{-}(NO_2)_3 . C_6H_2$, is a yellow solid with melting point 121° C. It is made by the nitration of phenol which has previously been treated with sulfuric acid to form phenol disulfonate; to the 50 per cent solution of the sulfonated phenol, placed in a number of earthenware pots, 65 per cent nitric acid is added at a very slow rate. The temperature rises and remains elevated for some time because the pots are packed in sand; the reaction proceeds to its

[11] "Nitrated cellulose" is correct, while "nitrocellulose" is incorrect, but the distinction is rather fine; the name is too well established in several industries to make a change advisable.
[12] Formula and preparation will be found in Chapter 27.
[13] The British standard smokeless powder.
[14] The complete analysis is: CO 28.5 per cent; CO_2 19.1; CH_4 11.2; NO 8.8; N_2 8.6; H_2O 22.0.
[15] Products from lower-nitrated cellulose in Chapter 35.

end, after which the pots cool. The picric acid separates in the form of yellow crystals; the spent acid is run off, and the crystals washed in large volumes of water, filtered, and dried at a moderate temperature. The formation of lead picrate must be avoided, for it is 5 times more sensitive than picric acid. The dried picric acid may be packed into shells or it may be melted with an added substance which lowers the melting point considerably; the lower temperature is safer.[16] Picric acid may also be made by the action of sodium nitrate and sulfuric acid on phenol.

Trinitrotoluene, TNT, 1-CH_3-2,4,6-$(NO_2)_3$. C_6H_2, has about the same explosive properties as picric acid, but possesses a lower melting point (81° C.), and is free of acid properties; this is an important advantage, since dangerous metallic derivatives cannot form. The nitration is performed in three steps, in a steel vessel with coils. First the liquid mononitrotoluene is made by using a mixture of 93 per cent H_2SO_4 (3 parts) and 75 per cent HNO_3 (2 parts); the spent acid is removed, and a mixture of 93 per cent H_2SO_4 and 85 per cent HNO_3 added, with heat and stirring; dinitrotoluene forms as an upper layer. On cooling, it solidifies to a pale yellow mass. The final steps consist of dissolving the dinitrotoluol (1 part) in 93 or 95 per cent H_2SO_4 (4 parts) and 90 per cent HNO_3 (1½ parts), with cooling at first, later with heating at 90° C., until the evolution of gas stops (3 hours). The solid is washed and recrystallized from alcohol, giving pale yellow crystals. The yield is 80 per cent. By means of additions and the application of pressure a mass resembling the nitrocellulose jelly may be prepared. The advantage of nitrating in steps is that the waste acid of one step serves as the nitrating acid of the preceding step. On detonating, some free carbon is formed, causing a black cloud.[17]

Ammonium nitrate is mixed with TNT in order to lower the cost, also as an oxidizer; by itself it can be detonated only with difficulty, but mixed with TNT, the mixture is stronger than pure TNT, and is easily detonated. Ammonium nitrate is made by adding sodium nitrate to a hot solution of ammonium sulfate; sodium sulfate separates out, for the greater part; the ammonium nitrate [18] is crystallized from the slightly diluted liquor.

$$2NaNO_3 + (NH_4)_2SO_4 = Na_2SO_4 + 2NH_4NO_3.$$
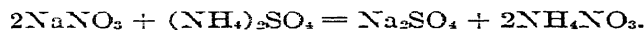
Ammonium nitrate is also made from odds and ends of nitric acid by neutralizing with ammonia.

Potassium chlorate, $KClO_3$, and perchlorate, $KClO_4$, form the basis of some high explosives, usually containing 75 per cent chlorate, 15 per cent dinitronaphthalene, some other suitable nitro derivative, and 6 per cent castor oil to reduce the sensitiveness to a safe limit.

Nitroguanidine, $NH_2 \cdot C:(NH) \cdot NH \cdot NO_2$, obtained, for example, by dissolving guanidine nitrate in concentrated sulfuric acid, and then dilut-

[16] One part picric acid and 1 part nitronapthalene mixed melt at 49° C.

[17] The complete analysis is: CO_2 3.7 per cent; CO 70; N_2 20; H_2 1.7; C 4.

[18] "Effecting and controlling crystallization of ammonium nitrate," J. Esten Bolling, *Chem. Met. Eng.*, 20, 401 (1919).

ing, has been used as an explosive. A flashless powder (reported by Giua) contained 50 per cent ammonium perchlorate, 40 per cent nitroguanidine, and 10 per cent pitch. There are countless other explosive mixtures, with a variety of names, and many of them patented.

The propellant charge of the cartridge is detonated by means of a sensitive mixture, such as 85 per cent fulminate of mercury, $Hg(CNO)_2$, and 15 per cent potassium chlorate, with or without powdered glass; stibnite may also be added. In the 3-inch shell and in larger sizes, the fulminate cap flashes into the main priming charge, black powder, which in turn ignites the propellant. The fulminate is made by dissolving mercury in 60 per cent HNO_3, and adding alcohol to the solution; the fulminate forms with heat evolution, and separates as a gray powder, which must be washed and dried at a low temperature. Fulminate is as sensitive as pure nitroglycerin, twice as sensitive as nitrocellulose, and 11 times as sensitive as TNT.

Lead azide is made from sodium azide; the latter is formed when nitrous oxide is passed over sodamide.

$$NaNH_2 + N_2O = NaN_3 + H_2O.$$
$$2NaN_3 + Pb(NO_3)_2 = Pb(N_3)_2 + 2NaNO_3.$$
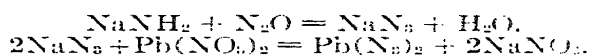
Lead azide is half as sensitive as fulminate.

INDUSTRIAL EXPLOSIVES

The explosives used for peace-time purposes, the industrial explosives, are chiefly dynamite, a high explosive, black powder, a mild explosive, and mixed explosives, such as the ammonium nitrate mixtures.[19]

To these might be added nitrostarch, a slightly yellow powder, made by nitrating starch with mixed acid.[20] Liquid oxygen[21] with charcoal is also an industrial explosive. The characteristics of the permissible explosives have been given in the introductory paragraphs.

In 1922, there were manufactured and used in the United States 431,772,077 pounds of explosives, of which 39 per cent was black blasting powder, 48 per cent high explosives, and 11 per cent permissible explosives[22]; in 1920, the corresponding percentages[23] were 47, 43, and 10. The mining industries consume about 75 per cent of the explosives produced; coal mining requires about 80 per cent of the black powder and permissible explosives.

Nitroglycerin and Dynamites. Nitroglycerin is made by nitrating glycerin; by itself it is too sensitive; it was in an effort to reduce its sensitiveness that Nobel discovered dynamite, a solid, made by absorbing the liquid nitroglycerin in kieselguhr, a diatomaceous earth. Since then,

[19] Example: Ammonium nitrate 60 per cent, TNT 15 per cent, aluminum powder 18 per cent, charcoal 7 per cent.
[20] *Bur. Mines Bull.* **No. 219**, 88 (1923).
[21] "Liquid oxygen explosives," G. St. J. Perrot and N. A. Tolch, *Bur. Mines Bull.* **No. 349** (1932).
[22] *Bur. Mines Tech. Paper* **No. 291.**
[23] *Bur. Mines Tech. Paper* **No. 340.**

other fillers have been developed; in America, the dynamites do not contain kieselguhr, but mainly wood meal, with sodium nitrate addition. The strength of the dynamite depends mainly on the content of nitroglycerin: 75 per cent is the highest, other grades have 20, 40, and 60 per cent. Special grades are made to specifications. The effect of the wood meal (or kieselguhr) is to cushion the dynamite, so that ordinary transportation shocks do not disturb it; it is packed in parchment paper "cartridges," not in metal boxes, for the same reason. The cartridges are packed in sawdust in wooden boxes, and one of these boxes dropped from a height on rocks below will not explode.

A very pure grade of glycerin [24] is used. The composition of the nitrating acid, of the spent acid, and the proportions taken are shown in the table below:

For each 100 pounds of glycerin, there are taken and obtained:

	Nitrating Acid			Spent Acid		
H_2SO_4	480	pounds,	60% of the nitrating acid	480	pounds	73.5%
HNO_3	273	pounds,	34% of the nitrating acid	67.6	pounds	10.3%
H_2O	47	pounds,	6% of the nitrating acid	105.7	pounds	16.2%

The recovery is 220 pounds of nitroglycerin, of the 246.7 pounds possible. The reaction is:

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(NO_3)_3 + 3H_2O;$$
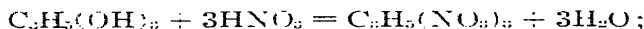
it is performed in a lead tank with numerous cooling coils, a sloping bottom, and a conical top with side outlet. Cocks are avoided, as their operation has caused accidents in the past; the nitrated product which floats on the acid is lifted by feeding in more acid, till it overflows at the side outlet of the conical top. Some acid is put in first, then some glycerin and the two stirred by a current of compressed air; gradually more of both are fed in; cold water in the coils maintains the temperature below 23° C. The product is washed in a lead tank with several changes of water, by means of air agitation; next it is washed with soda ash solution, and again with water; finally it is run through a mat of sponges to remove water droplets and is then ready to be mixed with the wood meal or kieselguhr. The charge per nitrator varies, but may be as high as 750 pounds per batch; the time for each cycle is about 4 hours.

The spent acid must be diluted slightly to prevent after-nitration of glycerin remaining in solution.

The dynamite is made in small batches; the wood meal and sodium nitrate are weighed into rubber bags and to each, the weighed amount of nitroglycerin is added and mixed by hand. The mixture is sieved and packed into the parchmentized paper by an automatic filling machine. Wood meal dynamite is yellow (kieselguhr dynamite also), and looks slightly wet.

A dynamite cartridge may be fired by an electrical spark, passed into a copper detonating cap which is slipped into the paper covering; the

[24] Chapter 32.

spark explodes a priming mixture bead similar to a match head; this in turn explodes a small store of fulminate in the copper capsule, which then sets off the dynamite.

Nitroglycerin solidifies at 13° C., and frozen nitroglycerin is difficult to explode, while the operation of thawing it, with haphazard equipment, is dangerous. A non-freezable dynamite is therefore made by mixing 20 parts of glycerin dinitromonochlorohydrin.[25] which remains liquid at −30° C., with 80 parts of nitroglycerin.

Recently ethylene glycol, $CH_2OH.CH_2OH$, made from ethylene, C_2H_4, has been nitrated on the large scale and successfully introduced in the explosive industry (Chapter 25).

Black Powder. Black powder, often called gunpowder, is no longer the military propellant; for it is too weak, and it develops a cloud of smoke; its products of decomposition are 44 per cent gaseous and 56 per cent finely divided solids.[26] It is mainly an industrial explosive now, for coal mining particularly, but it still renders service in military explosives: in the primers for rapid-firing artillery and navy guns, as the intermediate explosive between the fulminate and the main charge of smokeless powder; in the high-explosive shells as time fuse, and in the shrapnel shell. In coal mining it is the main charge, and also forms the core of the fuse.

Black powder of standard composition contains 75 per cent potassium nitrate, 15 per cent charcoal, and 10 per cent sulfur; in the United States, sodium nitrate is substituted for the potassium salt, in about the same percentage. The three ingredients are powdered separately, then mixed together in an edge runner,[27] with the addition of a little water; the mass is next compressed, granulated, and sieved. The blasting cartridge is a single cylindrical piece formed by pressing, with one perforation (in the long axis).

There were produced in 1935:

	Pounds	Value per pound in cents
Dynamite	337,978,213	10.2
Permissible explosives	47,990,826	10.2
Nitroglycerin	2,483,262	
Blasting powder	35,153,125	6.11
Pellet powder	31,467,150	6.6
Gunpowder, black, and smokeless	28,215,211	16.5

OTHER PATENTS

1,849,356, an explosive nitrocellulose grain surface treated with tetranitroaniline; 1,775,271, a nitroglycerin cell, container for charge in shooting wells; 1,814,980, manufacture of TNT; 1,868,388, on diethylglycol dinitrate (A. Hough); 1,828,788, improved explosives of the dynamite and gelatin type; 1,820,567-8, explosives consisting of sodium chlorate, sodium nitrate, TNT, ortho-nitrotoluene and sawdust; 1,819,457, process of making a colloidal starch explosive.

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[25] $CH_2Cl.CH(NO_3).CH_2(NO_3)$, made by nitrating glycerin monochlorohydrin, $CH_2Cl.CH(OH).CH_2(OH)$.

[26] The solids are K_2CO_3 or Na_2CO_3 about 60 per cent; sulfate about 15 per cent; sulfide about 13 per cent; and sulfur.

[27] Chapter 44.

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During the World War, chemicals were extensively used for the first time to incapacitate or harass troops and to form screens for masking troop movements and operations. Protection from these chemicals was obtained also by the use of chemicals. A further protection against chemicals in warfare is the understanding of them, for man fears most that which is mysterious to him. Huge quantities of these war chemicals are required for effective military operations so that large-scale facilities for their manufacture must be maintained in peace time, just as plants and their staffs are maintained for the manufacture of guns and explosives. Even more important than physical equipment, however, is detailed information concerning the most efficient methods for the manufacture of the required chemicals, and the training of men to know and use them in the field.

Chapter 34

Chemical Factors Other than Explosives in Warfare*

The use of poison gases by the German army at Ypres on April 22, 1915, marked a new era in modern warfare. The popular opinion is that this form of warfare was original with the Germans; such, however, is not the case. In milder form, chemicals have been used in warfare for many centuries. The first recorded effort to overcome an enemy by the generation of poisonous and suffocating gases seems to have been in the wars of the Athenians and Spartans (431-404 B. C.) when the latter besieged the cities of Platea and Belium. The attackers saturated wood with pitch and sulfur and burned it under the walls of these cities in the hope of choking the defenders and rendering the assault less difficult. Similar uses of choking and poisonous gases are recorded in the history of the Middle Ages.

In the attack of April 22, 1915, the German army made use of chlorine discharged from stationary steel cylinders; the cloud of chlorine gas was carried along by the wind. It was found that a cloth bandage steeped in sodium thiosulfate (hypo [1]), and wrapped over the nose and mouth, gave fair protection against chlorine. These bandages do not protect the eyes, so that when the enemy sent over tear gases or lachrymators in shells, much damage was done. The lachrymators are used in shells because they are liquids at ordinary temperature and do not pass into vapor form rapidly enough to be used in cylinders. In chemical warfare parlance the word gas is used in a broad sense, and denotes any substance, solid, liquid, or gas, which is dispersed in the air and which irritates the lungs, eyes, or skin. Protection against tear gases was given by hoods

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[1] Chapter 4.

with eye-pieces; the hoods could be impregnated with suitable chemicals; later, regular masks were developed.

The gas used by the German army from April to June, 1915, was commercial chlorine, but in December of that year, a mixture of chlorine and phosgene was introduced. Phosgene is seven times as toxic as chlorine, is harder to neutralize, and has a delayed action which makes it still more effective. To absorb phosgene, the British hoods and the first French masks were impregnated with a solution of sodium phenolate and hexamethylenetetramine. The British changed after a time from the hood or helmet, as it was called, to an impervious mask with a box respirator (canister) attached.

The next development in the offense was the use of chloropicrin in shells which scattered their liquid charge by the explosion of the "booster." Chloropicrin, $CCl_3 . NO_2$, is a liquid boiling at 112° C., much less toxic than phosgene, but distinctly lachrymatory. It causes vomiting; this effect makes it difficult for the soldier to keep on his mask.

In July 1917, the German army began using mustard gas, a liquid boiling at 219.5° to 228° C., which attacks the skin as well as the lungs and eyes, causing bad burns which may incapacitate a soldier for a number of weeks. While the mask protects the face satisfactorily, the problem of protecting the whole body is a serious one. Special ointments and special clothing were devised at once, but were not really satisfactory at the time the armistice was signed.

Another type of chemical agent of importance in warfare is the so-called sneeze gas, diphenylchloroarsine. This is a high-melting solid which is dispersed as a very fine smoke or dust by means of high explosives. In order to protect satisfactorily against this toxic smoke, special filtering pads are employed.

It was also found that toxic smokes could be more effectively dispersed by heat; this is accomplished by mixing substances such as diphenylchloroarsine with smokeless powder and igniting with suitable starting and match-head compositions.

CLASSIFICATION

The various chemical agents employed for the production of casualties may be classified according to their physical properties, their tactical use, or their physiological effects. It has already been stated that chemical warfare agents may be solids, liquids, or gases at ordinary temperature. Depending upon physical condition and physical constants, particularly the vapor pressure, chemical warfare materials are also classified as persistent and non-persistent. Gases in general are non-persistent, while liquids and solids are apt to be persistent, due to slow volatilization. Thus chlorine and phosgene are non-persistent, due to quick volatilization, while chloropicrin, a liquid even at summer temperatures, is more persistent. Mustard gas has a still higher boiling point and is highly per-

-sistent, while the solid substance chloroacetophenone will persist for weeks or months. Solids that have become vaporized as smokes behave like gases and are relatively non-persistent.

The tactical use of chemical warfare materials is largely governed by this property of persistency. Thus non-persistent chemical agents such as phosgene are employed against positions to be attacked shortly afterwards, whereas persistent chemical agents such as mustard gas are employed to harass the enemy or to render positions untenable.

The chemical agents are classified physiologically as follows:

(a) Agents which produce their effects through inhalation:
   (1) Asphyxiants and respiratory irritants such as phosgene and mustard gas.
   (2) Nauseating gases: Diphenylaminechloroarsine, or chloropicrin.
(b) Lachrymators or tear gases: Bromobenzyl-cyanide or chloroacetophenone.
(c) Vesicants or skin-blistering agents: Mustard gas.

In many instances a single chemical agent may be capable of producing a number of different physiological effects; thus, mustard gas is classed both as an irritant and as a vesicant; to some extent it is also a lachrymator, as are most of the chemical agents which produce physiological effects.

TABLE 68.—*Casualty-Producing Chemical Agents.*

Chemical Agent	B. pt. ° C.	Physical State	Physiological Action*	Method of Projection
Chlorine (Cl_2)	−33.6	Gas	l,ri	Cylinders
Phosgene ($COCl_2$)	8.2	Gas	l,ri	Cylinders, shell, bombs
Chloropicrin (CCl_3NO_2)	112.0	Liquid	ri,tg,e	Shell
Superpalite (CCl_3COCl)	128	Liquid	l,ri	Shell
Mustard gas ($CH_2Cl.CH_2)_2S$..	219.5	Liquid	l,ri,v	Shell, bombs
Lewisite ($CHCl:CHAsCl_2$)....	190	Liquid	l,ri,v	Shell
Bromoacetone ($CH_2BrCOCH_3$)	126	Liquid	lach,tg	Shell, bombs
Bromobenzyl-cyanide ($C_6H_5CHBrCN$)	242	Liquid	lach	Shell, bombs
Chloroacetophenone ($C_6H_5CO.CH_2Cl$)	247	Solid	lach	Shell, candles, grenades
Diphenylchloroarsine ($C_6H_5)_2.AsCl$	383	Solid	i,e	Candles, shell

*l = lethal, ri = respiratory irritant, i = irritant, e = emetic, tg = tear gas, v = vesicant, lach = lachrymator.

Table 68 lists the more important chemical agents employed in the World War for the production of casualties and also gives for each some of the physical properties, physiological effects, and the type of container (shell or bombs) used for their dispersion. It will be noted that all of the chemical agents listed contain either chlorine or bromine, so that it appears probable that one or more halogen atoms are necessary in casualty-producing chemical agents.[2] Practically all these chemical agents can be loaded into steel projectors or containers without danger of corrosion, except the bromine compounds, which attack steel; shells lined with lead or enamel must then be used. It was to avoid the special lining that a

[2] Hydrocyanic acid gas, or hydrogen cyanide, HCN, is an exception; it was not found effective in the field, however, because it dissipated too rapidly.

FIGURE 183.—Two aëroplanes laying a smoke curtain around a bombing target. (Courtesy of the U. S. Army Air Corps.)

suitable substitute for bromobenzyl-cyanide was sought. As a result of this search, chloroacetophenone was discovered; it does not attack steel and is as effective a lachrymator as bromobenzylcyanide.

Medical Aspects. All of the casualty-producing chemical agents are lethal in sufficiently high concentrations, but it is difficult to reach such high concentrations in the open; many of them, however, produce light casualties in very low concentrations and it is for this reason that chemical agents have been found to be so effective in warfare. That the casualties are mainly light is clearly brought out by the report of the Surgeon General of the United States Army in 1920, which shows that 27.3 per cent of all the United States Army casualties during the World War were gas casualties, but all except 2 per cent of these were temporary casualties and recovered. On the other hand, approximately 25 per cent of all casualties produced by weapons other than gas, failed to recover. It follows that a man who was injured by gas had twelve times as many chances for recovery as the man who had been injured by shell fire, bullet, or bayonet.

The chemicals used in chemical warfare injure by direct irritant and burning action to the skin and mucous membranes with which they come in contact. Such chemicals are powerful germicides and as a result, the wound is sterile. Some of the warfare chemicals have a pronounced irritant action on the mucous membrane of the upper respiratory tract, yet have little effect on the lungs proper. Others have only a light irritant action on the respiratory tract, but have a strong burning effect on the lungs; while still others possess irritant and burning properties in nearly equal degree. For these reasons, contrary to wide-spread belief, there are few after-effects among those wounded by gas or chemicals, provided they had ordinary body resistance.

SMOKE SCREENS

In addition to the production of casualties, chemical agents were also extensively employed for producing smoke screens, incendiary effects, and in gas-mask canisters for the absorption of the casualty-producing agents.

The most effective smoke-producing chemical is white phosphorus which ignites spontaneously in contact with air, producing a dense white smoke. Phosphorus for this purpose is used in shells, grenades, or bombs. Other important smoke-producing materials are sulfur trioxide in the form of oleum, stannic chloride, and titanium tetrachloride; these three chemical agents produce white smoke as a result of contact with the moisture in the atmosphere. They were employed in shells and grenades. Since the war titanium tetrachloride has come into extensive use for the production of screening smokes sprinkled from aeroplanes. The other important smoke materials were the zinc-containing mixtures which were used in a smoke box, in smoke candles and in certain of the smoke grenades. One such mixture has the composition:

Zinc	34.6	per cent
Carbon tetrachloride	40.8	
Sodium chlorate	9.3	
Ammonium chloride	7.0	
Magnesium carbonate	8.3	

This mixture when ignited produces a light gray smoke of high obscuring power. A smoke box may be dropped behind a fleeing vessel, and burns for 9 minutes.

Various chemicals were employed during the war as incendiaries chiefly in the form of aeroplane bombs; one type contained thermite, a mixture of aluminum powder and iron oxide, surrounded by oil set to a jelly with a small amount of soap; another type contained white phosphorus (Chapter 7) in fuel oil, which provides for spontaneous combustion on contact with air.

The chemicals employed in the gas-mask canister are charcoal and soda lime. The charcoal is an especially activated product prepared from nut shells. It absorbs practically all gases to some extent but is specially active in the absorption of the vapors from liquids; it acts catalytically also, thus for phosgene which is decomposed by water vapor at a slow rate ordinarily, the speed is increased so that the phosgene is destroyed as fast as it enters. The harmless substances carbon dioxide and hydrogen chloride are formed, and these are completely absorbed by a layer of special soda-lime.

$$COCl_2 + H_2O = CO_2 + 2HCl.$$
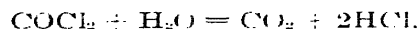
Sodium permanganate or some other oxidizer is also present in the canister, as well as cotton wool or paper pulp for filtering out dusts.

Most of the chemical warfare agents were known prior to the World War, but many of them had been made in the laboratory only, in small lots. Manufacturing processes had to be developed and plants erected under war pressure. The manufacture of gas-masks with canisters was an even more pressing matter, for without them the men in the trenches were helpless against the new weapon. The task was so well accomplished that when the war ended, the allies had a decided advantage in materials for offense as well as defense.[3]

PROCESSES OF MANUFACTURE

Phosgene is made by the catalytic combination of carbon monoxide, CO, and chlorine.

The catalyzer consists of carbon granules, and acts in two stages. A first iron box, 8 feet long, 2 feet 9 inches deep, and 11 inches wide, is set in cold water; in this box the conversion takes place to the extent of 80 per cent. A second box, to which the gas from the first box passes, is surrounded by hot water, and here the conversion is completed. The reaction is: $CO + Cl_2 = COCl_2$, phosgene. The finished material in gas form is dried by means of sulfuric acid towers, and is liquefied by passing

[3] Most of the chemists for the Chemical Warfare Service were university professors and instructors.

it through lead coils laid in brine.[4] The liquid phosgene is run into iron containers previously evacuated and cooled. From these it may later be run into shells cooled to $-20°$ C.; the filling stations for this purpose are situated under hoods with fans, so that the escaping gas is drawn away and discharged into the atmosphere, or destroyed in scrubbing towers.

Phosgene is also a commercial chemical; it is used in organic reactions.

Mustard gas, dichlorodiethylsulfide, $CH_2Cl . CH_2 . S . CH_2 . CH_2Cl$, is made by passing ethylene, C_2H_4, into sulfur monochloride, S_2Cl_2:

$$2C_2H_4 + S_2Cl_2 = (CH_2Cl . CH_2)_2 S + S.$$
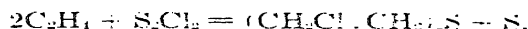
There is formed at the same time free sulfur, as indicated in the equation, and the removal of this sulfur caused much difficulty until it was found that by running the reaction at $30°$ C., most of the sulfur remained in colloidal solution, and need not be separated at all. The product containing colloidal sulfur is nearly, if not quite, as active as pure mustard gas.

Ethylene for such emergencies is prepared by passing alcohol in vapor form over kaolin heated to $500°$ or $600°$ C.; $C_2H_5OH = C_2H_4 + H_2O$.

Sulfur chloride is made in cylindrical steel tanks laid on their sides; a batch of sulfur is placed in the tank, melted by the application of outside heat, and dry chlorine passed in. As the reaction proceeds, $2S + Cl_2 = S_2Cl_2$, heat is evolved, and the tank must be cooled by a spray of water. After all the sulfur is converted, the sulfur chloride, a liquid with a characteristic odor, is run off and another batch started.

The sulfur chloride and ethylene are combined in the presence of mustard gas from a previous batch, which acts as a solvent, in the Levinstein reactor (English). The product is run to settling tanks, where a small amount of sulfur and sludge settles out; the supernatant liquid is pale yellow, and is ready for shell filling without further treatment. Pure mustard gas is a solid which melts at $13°$ C.; the product made as described contains impurities which lower the melting point.

Chloropicrin. In order to manufacture chloropicrin, $CCl_3 . NO_2$, steam is passed through a mixture of calcium picrate and bleaching powder. The calcium picrate is made by neutralizing picric acid (Chapter 33) with lime.

Bromobenzyl-cyanide. The most effective lachrymator is probably bromobenzyl-cyanide, $C_6H_5 . CHBr . CN$, a liquid at summer temperature. The manufacture consists of the following steps: Benzyl chloride, $C_6H_5 . CH_2 . Cl$, made by chlorinating toluene at $100°$ C., is mixed with an equal volume of 50 per cent alcohol, and treated with sodium cyanide; sodium chloride and benzyl cyanide, $C_6H_5 . CH_2 . CN$, form. The cyanide is subjected to fractional distillation and the fraction boiling within 3 degrees of the boiling point $(231.7°$ C.) is treated with bromine vapor mixed with air; the reaction is catalyzed by a small amount of bromobenzyl-cyanide from a previous batch. The product obtained is freed of the hydrogen bromide formed at the same time by a stream of air,

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[4] By using a slight excess of carbon monoxide, practically all the chlorine is made to react; the excess carbon monoxide does not liquefy and is vented at the discharge point.

and is then sufficiently pure for use as a lachrymator. It has a low vapor pressure and thus is highly persistent.

Chloroacetophenone, $C_6H_5 . CO . CH_2Cl$, a solid, as effective a tear gas as bromobenzyl-cyanide, is produced from acetic acid, chlorine, and benzene. Acetic acid is chlorinated to form monochloroacetic acid, $CH_2Cl . COOH$; this compound is then treated with chlorine and sulfur monochloride to form chloroacetylchloride, $CH_2Cl \cdot CO \cdot Cl$. The final step is the treatment of chloroacetylchloride with benzene in the presence of aluminum chloride to form chloroacetophenone.

Lewisite [5] is a vesicant similar to mustard gas. The process for its manufacture was not developed in time for use during the World War. Acetylene is bubbled through a mixture of anhydrous arsenic trichloride and aluminum chloride; absorption is rapid and much heat is developed. The reaction produces a heavy liquid consisting of three main fractions: the lower boiling one is Lewisite, a faintly yellow liquid, with composition $CHCl: CH . AsCl_2$, chlorovinyldichloroarsine.

Diphenylchloroarsine, the sneeze gas applied in the form of atomized solid, is made from diazotized aniline and sodium arsenite; numerous reactions are involved.[6]

CHEMICAL ABSORBENTS

The chemical absorbents employed in the gas-mask canister for eliminating casualty-producing agents were soda-lime and charcoal; special processes for their production were developed during the war. For the production of suitable soda-lime, the method consists of making a plastic mass of lime, cement, kieselguhr, caustic soda, and water, spreading it in slabs on wire-bottomed trays, allowing it to set two or three days under carefully-controlled conditions, drying, grinding, and screening to 8- to 14-inch mesh, and finally spraying with a solution of sodium permanganate with a specially designed spray nozzle. A representative composition of such soda-lime would be:

	Per cent
Hydrated lime, $Ca(OH)_2$	55
Portland cement	17
Kieselguhr	7.2
Sodium hydroxide, NaOH	1.2
Sodium permanganate, $NaMnO_4$	3.8
Moisture	15.7

The lime is the essential constituent for absorption. The cement renders the granules hard so that they do not form dust while the canister is in service; such dust would soon clog the canister. The loss in absorptive capacity due to the presence of the cement is in part counterbalanced by the introduction of the bulky kieselguhr. Sodium hydroxide increases the activity of the granules, and serves also to maintain the proper moisture content. This moisture content is very important in order to secure

[5] Green and Price, *J. Chem. Soc.*, **119**, 448 (1921). Lewisite is named after Professor W. Lee Lewis of Northwestern University.

[6] "Chemical warfare," Fries and West, New York, McGraw-Hill Book Co., 1921, p. 183, and J. Norris, *Ind. Eng. Chem.*, **11**, 825 (1919).

maximum gas absorption. The function of the permanganate is to oxidize arsine and similar compounds.

The charcoal[7] was made by carbonizing coconut shells, and for lack of sufficient coconut shells, by carbonizing fruit pits, walnut shells, hard wood, spruce, and even anthracite. The charcoal found most efficient in absorption was coconut charcoal, the efficiency of the others varying in the order given, but all charcoals become useful, rapid absorbers only after activation by a steam, or steam and air treatment. The preparation of an activated charcoal, then, involves two steps: The formation of a porous amorphous base carbon at a relatively low temperature, followed by the removal of adsorbed hydrocarbons from the primary carbon, thereby increasing its porosity. The first step presents no serious difficulties since it simply involves a distillation at relatively low temperature. The second step is a much more difficult matter. The procedure which has yielded best results is to remove the adsorbed hydrocarbons by combined oxidation and distillation involving steam alone, or steam and air; the hydrocarbons of high boiling points are broken down into more volatile substances easily removed at low temperatures and under conditions less likely to result in the deposition of the secondary carbon, which is inactive. During the removal by oxidation and distillation of the hydrocarbons, a loss in primary carbon by oxidation occurs; the condition of activation must therefore be so chosen that the hydrocarbons are oxidized rapidly, the primary carbon slowly.

In the steam-activation process, the charcoal is placed in an upright steel tube with top feed and bottom discharge; the tube is surrounded by fire gases which maintain its temperature at 800° to 1000° C. Superheated steam enters through an inner tube and streams downward through the charcoal, carrying away the undesired hydrocarbons before they can be decomposed by the high temperature and deposit inactive carbon. A certain amount of oxidation also takes place, for after the original carbonization, the charcoal is exposed to air which is absorbed and thus carried into the activating chamber.

In the steam and air treatment, the temperature is 350° to 450° C.; the product is about the same as for the steam activation; each method has certain advantages.

Before activating, the charcoal is ground and sieved to the same size as the soda-lime granules.

The activity or absorption power of the charcoal is determined by passing a standard concentration of some gas, such as chloropicrin, mixed with air, through a tube containing a standard amount of charcoal; the period of time which elapses before the chloropicrin appears in the exit gases is a measure of the absorption power. An unactivated charcoal absorbs the chloropicrin from a 1 per cent mixture for about 2 minutes only, while activated coconut charcoal absorbs for 58 minutes. The coconut charcoal produced during the war on the large scale was good for about 34 minutes under this test. The concentration of the test gas is

[7] *Ind. Eng. Chem.*, **11**, 95 (1919).

much higher than that of the gases normally encountered in the field in warfare, so that the service of the gas mask canister is very much longer (say 100 times) than would appear from this test. Besides the soda-lime and charcoal absorbents, the canister [s] contains cotton pads for retaining dusts.

BY-PRODUCTS OF CHEMICAL WARFARE

Chemical warfare research and development have also resulted in many discoveries which are of vital importance in connection with the peaceful pursuits of the country. These by-products of chemical warfare include: the use of chlorine as a cure for colds; the use of chloropicrin as an insecticide for treating stored grain; the use of cyanogen chloride with hydrocyanic acid for the fumigation of ships and warehouses, valuable because cyanogen chloride is a tear gas as well as a fumigant and serves as warning that dangerous concentrations of hydrocyanic acid gas are present; the use of tear gas for the control of mobs, and the subjection of criminals; and the adaptation of the army gas mask for the protection of those who manufacture or use industrial poisonous gases and dusts. The industrial gas masks are similar to the army gas mask except that special canister absorbents are employed to afford protection against the particular industrial poison or noxious gas which may be encountered; there is also an all-purpose canister which affords protection against all poisonous gases and smokes which might be encountered by firemen in fighting fires. (Compare also p. 639.)

Chemical warfare research is therefore of importance not only to provide national defense in the event of war involving the use of chemical agents, but also to provide knowledge concerning the effective use of industrial poisons, and to furnish methods of protection for those who may encounter such poisons in their work.

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"War gas investigations," Van H. Manning, *Bur. Mines Bull.* No. **178A**, 1919.

"The research division, chemical warfare service, U. S. A.," George A. Burrell, *Ind. Eng. Chem.*, **11**, 93 (1919).

"Production of gas defense equipment for the army," Bradley Dewey, *Ind. Eng. Chem.*, **11**, 185 (1919).

"Gas offense in the United States," *Ind. Eng. Chem.*, **11**, 5-11 (1919), an article with 23 illustrations.

"Chemical warfare service saves millions for industry," R. E. Sadtler, *Chem. Met. Eng.*, **37**, 88 (1930).

[s] A canister with one side replaced by glass so that the contents are visible may be purchased for a small sum from the Mines Safety Appliances Company, Pittsburgh, Pa., and is well suited for exhibition in the class-room or museum.

In scientific laboratories, the researcher quite naturally seeks to obtain crystallizable solids, rather than non-crystallizable ones, generally dubbed "tars." By means of crystallization, he can purify his new substance; on pure substances alone can the constitution of its molecules be settled beyond doubt. The synthetic resins have afforded the first big lesson to the chemical investigator, that the humble "tars" may have their uses. With other chemical discoveries, that of the synthetic resins has meant, and still means, increased capacity for service to man on the part of the science, mainly in new directions.

Chapter 35

Synthetic Resins, Natural and Synthetic Phenol. Celluloid, Casein Plastics

Under the term synthetic resins there is grouped together a growing number of non-crystallizing, organic materials of synthetic or semi-synthetic origin, which resemble the natural resins in appearance, and speaking very generally, in properties. The synthetic resins are either amber-colored, or water-white solids, insoluble in water, soluble in organic substances, and fusible. The products marketed by the synthetic resin manufacturer are in an unfinished state; the fabricating plant or specialty plant is the place where they are transformed so that they acquire the insoluble, infusible, lustrous state, which is the state in which the general public knows them. This transformation is called "curing," and involves the use of heat and pressure.

The uses for the synthetic resins divide them into two main classes: those which serve as plastics,[1] giving after molding and curing the products of numerous shapes; those whose uses are similar to the uses for natural resins, that is, as film-forming substances in varnishes and protective coatings in general. The first group includes the resins in molding materials and the transparent resins; the second, the oil-soluble resins. In addition, synthetic resins function as adhesives and cements, and as impregnating fluids.

An older plastic, still very valuable, is Celluloid, a nitrated cellulose plasticized by camphor. Casein plastics serve for special purposes. They are discussed later in this chapter.

The material marketed by the resin manufacturer is termed the resinoid A; it is furnished a) as the pure resinoid in cast shapes, roughly approximating the form which they are to possess when finished; this finishing is done on equipment very similar to the ordinary wood-working equipment; b) in combination with a filler, commonly wood

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[1] Plastics are bodies which under the influence of heat and pressure become soft enough to be pressed, formed or shaped, while after cooling they are rigid again; or bodies which soften under the influence of heat and may be molded under pressure when so heated, but which harden in the period of heating, and after cooling may no longer be softened by heat; or bodies which made up with water are soft and may be shaped, retaining the shape permanently after the removal of the plasticizing water. The clays belong to the third class.

flour, as a molding material; c) as a solution of resinoid A (explained later) for laminating, that is, forming the adhesive or cement to many sheets of paper or cloth which together form a board. There must be added d) the oil-soluble resins, shipped in cans or drums, in the form of irregular pieces of small size.

The manufacture of resins require simple apparatus; the process consists as a rule in mixing two liquids, or a solid and a liquid, heating them together to produce the reaction, removing any water formed, then heating the product further with, or without, additions, until a test sample shows the proper melting point and viscosity. The end point is not definite, and a variety of intermediate products may be obtained. Uniform products are obtained only by taking the same quantities, heating to the same temperature for the same length of time, with all other conditions identical. Not only the length of cook, and temperature, but the absence, presence, and kind of catalyst influences the properties of the product.

The depth of color of the product depends partly on the degree of purity of the raw materials; in general, the darker these are, the darker will be the resin.

In order to produce synthetic resins at reasonable prices, raw materials must be available at low prices. The chief raw materials are urea, formaldehyde, phenol, phthalic anhydride, and glycerin; stimulated by the possibility for considerable consumption in the resin manufacture, the production or recovery of these materials has progressed sufficiently to insure abundant supplies at relatively low prices. The resins containing phenol, whether recovered or synthetic, or phthalic anhydride, may be considered as of coal-tar origin. The non-coal-tar resins are designated in the more detailed presentation which follows.

Synthetic Resins Leading to a Final Hard and Rigid Shape.[2]

The earliest synthetic resins were heat-hardening resins, called also *thermosetting plastics;* they soften under heat and pressure and undergo a chemical change which gives them a peramanently rigid form. Grouped according to their chemical origin, they are: a) phenol or cresol-formaldehyde condensation products, representing the *phenol resins;* b) urea-formaldehyde condensation products; c) thio-urea-formaldehyde condensation products; b) and c) are also designated as *amino resins:* d) phthalic anhydride and glycerin condensation products, representing the *alkyd resins,* which include all polybasic and polyhydric alcohol resins.

When used in the pure state, that is, without any admixture, the material is the "transparent material or resinoid"; admixed with fillers

[2] Examples: For a) Bakelite, Durez, Redmanol, Condensite, Resinit, Amberite, Formite, Phenoform, Nuloid, Amberdeen, Sipilite, Faturan. For b) Pollopas, Plastopal, Schellan. For c) Beetleware. For d) Glyptal, Rezyl. The use of a trade name in discussions may lead to errors, because such a name may be used to designate products with various formula. It is well to use instead the chemical group names.

such as wood flour, it becomes a molding material, of great importance, because of its superior qualities.

A number of resins or resinoids leading to hard, rigid final products are of the *thermoplastic type;* they soften under heat and pressure, but undergo no chemical change. Vinyl chloride resins, vinyl acetate resins, styrene resins, α-methacrylate resins, modified phenolics, and others, represent this class.

In general, the products of condensation are thermosetting resins, while the products of polymerization are thermoplastic resins.

(a) Phenol or cresol-formaldehyde condensation products. This development proceeded along three different lines, all leading to a final infusible resin. 1) Methods employing ammonia or a metallic base such as caustic soda as the catalyst.[3] 2) Methods using no condensing agent, but an elevated temperature, or else an acid catalyst, with the subsequent addition of hexamethylenetetramine;[4] and others, in which phenol,

$$\text{phenol} \quad \text{OH} \quad + \text{CHOH} \longrightarrow \quad \text{OH} \quad \text{CH}_2\text{OH}$$

phenol   *formaldehyde*   *hydroxybenzyl alcohol*
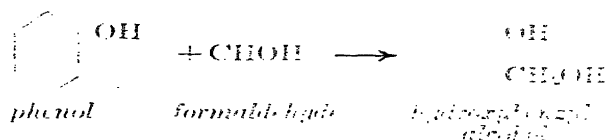
hexamethylenetetramine, and anisole are used, permitting an easier reaction;[5] in a later patent, the anisole is omitted.[6] 3) Methods in which hydroxybenzyl alcohols are consciously formed and condensed further with the addition of a base as condensing agent.[7]

By writing formaldehyde in its hydrated and no doubt true form when in solution, as methylene glycol, the reaction is clearly shown to be a condensation reaction, and it becomes more understandable: $\text{CHOH} - \text{H}_2\text{O} = \text{CH}_2(\text{OH})_2$, and

$$\text{phenol OH} \quad + \text{CH}_2 \begin{matrix} \text{OH} \\ \text{OH} \end{matrix} \longrightarrow \quad \begin{matrix} \text{OH} \\ \text{CH}_2\text{OH} \end{matrix} \quad - \text{H}_2\text{O}$$

phenol   *methylene glycol*   *hydroxybenzyl alcohol*
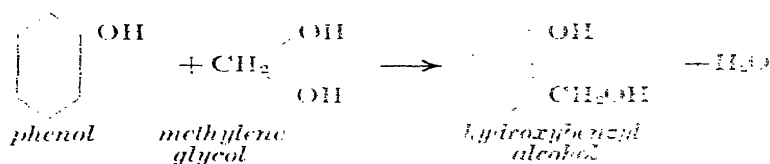
Procedure. In a general way, the procedure in these three methods is the same. The phenol in liquid form,[8] and the formaldehyde as 40 per cent solution, equal parts by weight, are placed together in a kettle fitted with a reflux condenser; the two liquids are miscible. 0.5 to 5 per

[3] U. S. Patent 942,809 (1909); the previous patent to Baekeland does not mention the catalysts. 942,699.
[4] U. S. Patent 1,020,593, the Aylsworth patent.
[5] U. S. Patent 1,209,333 (Redmanol).
[6] U. S. Patent 1,230,829 and U. S. Patent 1,310,088 (Redmanol).
[7] Brit. Patent 15,517 (1905), the de Laire patent.
[8] Phenol is solid melting at 40.8° C.; 2 per cent water liquefies it.

cent catalyst (on the weight of the phenol) is added, selected from a long list of materials, basic or acid, organic or inorganic. Gentle heat is applied, so that the liquid boils quietly. After 2 hours or so, the upper water layer which gradually separates has reached a maximum, and is run off. The lower thin-flowing liquid (while warm) is resin A, which on cooling hardens to a brittle solid, soluble in organic solvents.

The proportion of the reactants, and of the catalyst, may be varied; the catalyst may be acid or basic.

For casting-resinoids the "one-step" process is usually used. In this process the reactants are employed in theoretical proportions. They are heated in the presence of the catalyst until the resinoid separates. The supernatant water is removed, the resin dehydrated, and poured into molds. It is then polymerized under heat and pressure until it is infusible. These infusible cast shapes are sold to the trade to be cut, sawed, sanded, drilled, or turned, as desired, using equipment similar to that used in wood working. Pipe bits, beads, cutlery handles, and the like are thus made.

Resinoids suitable for molding are usually made by the two-step process. In this process the phenol is employed in excess. The reaction is similar to the one-step process. The fusible dehydrated resin is run into pans, cooled, then an intimate mixture of this fusible resin, with hexamethylenetetramine sufficient to render the fusible resinoid infusible when heated, and a filler, usually wood flour, are ground together in a ball mill. The resulting mixture constitutes the molding powder sold commercially. Such a powder charged into a steel mold and subjected to heat and pressure is changed to an infusible, rigid molded article. Closures, electrical equipment, telephone parts, automotive parts, and the like are thus manufactured.

If the dehydrated, unpolymerized, resinoid, as obtained from the one-step process, is dissolved in a solvent, it constitutes the varnish used for the impregnation of paper, fabric, or the like. If such impregnated paper or fabric is piled sheet on sheet to the thickness desired and the whole subjected to heat and pressure, there are produced so-called laminated plates, employed as panels, laminated gears, etc.

The influence of the catalyst on the properties of the product is profound: if the resin in state A contains a basic substance, or a salt, there is a change of composition with time; on heating, the same change is rapid, and the resin hardens (heat-hardening); if the resin A contains an acid as catalyst, the resin does not reach the heat-hardened state.

The earliest formula [9] to represent resin A, formed by 2 parts of formaldehyde and 3 parts of phenol, when heated to 400° F. (204° C.), without catalyst, is that of Aylsworth. The subsequent addition of 7.6 to 12 parts of formaldehyde-ammonia compound forms a fluid at 200° F. (93° C.), which when heated for a time gives an infusible, inert mass, without the production of bubbles (one of the difficulties in the early days). A formula for stage C follows:

[9] U. S. Patent 1,020,593 (1912).

$$CH_2 {< \begin{matrix} C_6H_5O \\ C_6H_5O \end{matrix}}; \quad 6 \left\{ CH_2 {< \begin{matrix} C_6H_5O \\ C_6H_5O \end{matrix}} \right. + CH_2.N_2 = 6 C_6H_5O.CH_2 \quad - 4NH_3$$
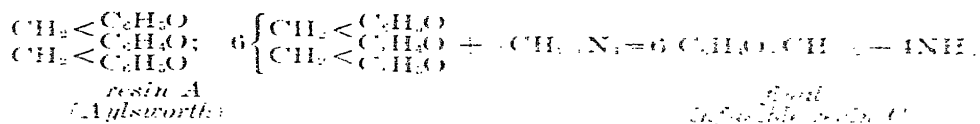
resin A
(Aylsworth)

Even before that, the patent of the French firm de Laire[10] had indicated that the resins obtained by heating phenol alcohols were the result of a condensation of several of these. The starting materials were phenol and hydrated formaldehyde, and the process of phenol-alcohol formation took place first, with the further condensation to an intermediate or final resin following.

$$\underset{CH_2OH}{OH} + \underset{CH_2OH}{OH} \longrightarrow \underset{CH_2}{OH} - \underset{CH_2OH}{OH} \quad - H_2O$$
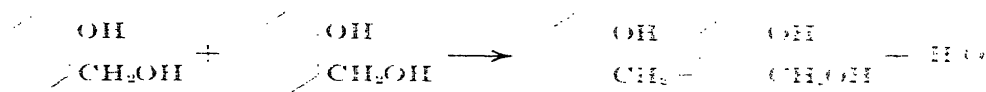
No separation of the phenol alcohols is made.

The formation of phenol alcohols was not recognized by the early scientific investigators of the phenol-formaldehyde reaction, because an acid catalyst was employed, which favors the condensation of the phenol alcohols, so that their presence escapes notice. With the introduction of alkaline catalysts, which catalyze only slowly the phenol-alcohol condensation, the presence of such alcohols was established.

With full consideration of the reactions of numerous substituted phenol and naphthol alcohols in mind, and leaning on the results of many experiments in which the relative amounts of phenol and formaldehyde were altered, Baekeland and Bender[11] gave the following as the probable reactions, and constitution, of the resin.

In the first step, the hydroxyl hydrogen of the phenol reacts, and partly rearranges to para-hydroxybenzene.

$$\underset{H}{\overset{H}{C}} = O + 2C_6H_5OH \quad \underset{H}{\overset{H}{C}} \underset{O.C_6H_5}{\overset{C_6H_4.OH}{}} + H_2O$$

$$\underset{H}{\overset{H}{C}} = O + \underset{H}{\overset{H}{C}} \underset{O.C_6H_5}{\overset{C_6H_4.OH}{}} - \to \underset{H}{\overset{H}{C}} = C \underset{O.C_6H_5}{\overset{C_6H_4.OH}{}} + H_2O$$

stage A

$$\underset{H}{\overset{H}{C}} = C \underset{O.C_6H_5}{\overset{C_6H_4.OH}{}} \quad \text{polymerizes to } (C_{14}H_{12}O_2)_n \text{ with small amount} \quad \left[\underset{H}{\overset{H}{C}} = C \underset{C_6H_4.OH}{\overset{C_6H_4.OH}{}} \right]$$
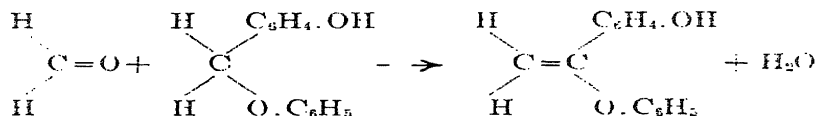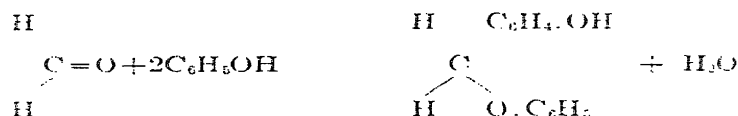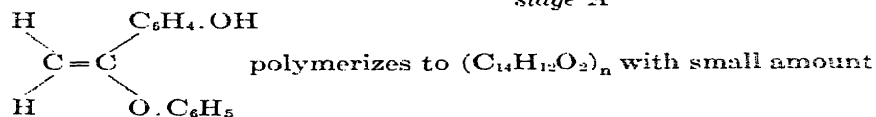
infusible resin
stage C
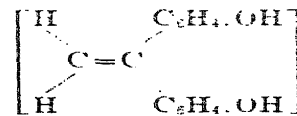
[10] Brit. Patent 15,517 (1905).
[11] *Ind. Eng. Chem.*, **17**, p. 225 (1925).

The final commercial product contains in addition to the polymers shown, small amount of unused phenol, formaldehyde, hexamethylene-tetramine, and traces of intermediate compounds. Resin B is a mixture of A and C; it is of scientific importance only.

Details of Manufacture of Resinoid A. Resinoid A is manufactured in either the "one-step" or the "two-step" process. About equal weights of commercial phenol and formaldehyde containing 30 per cent formaldehyde by weight, are placed in a kettle; 100 pounds of phenol is the usual batch. The amount of formaldehyde is adjusted so that there is a 1 to 1 molecule relation, with intentional variations (*see* below). Either no catalyst or a 1 per cent hexamethylenetetramine is added, and the whole heated 3 to 4 hours to 140° to 165° C. (284° to 329° F.); water is eliminated. In the one step process, the exact 1 to 1 relation, or excess formaldehyde is taken; the product is directly resinoid A. In the "two-step" process, there is a) excess phenol with an acid catalyst (say HCl), or b) excess catalyst, such as NaOH, later neutralized. For a) the second step involves adding more aldehyde and more catalyst, of basic nature; in the case of b), aldehyde and catalyst are added also.

The reaction between phenols and aldehydes will take any one of the following paths,[12] according to conditions:

(1) DIRECT RESINOID ROUTE ("One-step")

Theoretical or excess aldehyde present; either with or without catalyst (preferably basic)

(2) INDIRECT RESINOID ROUTE ("Two-step")

(*a*) Excess phenol present, either with or without catalyst (preferably mineral acid)

Fusible phenol resins ("Novolak" or "two step" resins)

Addition of aldehyde in presence of catalyst (generally basic)

(*b*) Excess catalyst present (preferably alkalies), followed by neutralization and heating

Fusible phenol alcohol resins (DeLaire type)

Removal of excess phenol and heating to high temperatures
or
addition of strong mineral acids

Saliretin resins (Kleeburg type)

Addition of aldehyde, basic catalyst, and a little phenol

Addition of aldehyde in presence of catalyst (generally basic)

Resinoid, "A" Type

[12] Reproduced from "Synthetic resins" by A. V. H. Mory, *Ind. Eng. Chem.*, **19**, 1110 (1927).

Resinoid A is distributed as stated in the introduction; a few words must be said regarding the preparation for molding compounds. For these, "an intimate mixture is prepared from the fusible resin (resinoid A) wood flour, and the desired coloring matter, if any, by grinding them together in a ball mill, hot-rolling the mass, again grinding, and screening, to insure absence of foreign matter."[13] To lesser extent, other fillers are used. "At the temperature given by 125 to 175 pound steam, such a molding material quickly fluxes, and then as quickly solidifies in the heat that first softens it."[13]

The color of the unmixed resin will reflect the quality of the phenol or cresol used; with very pure materials, it will be amber. With less pure materials, it may be brown, dark brown, or black. Dyes have been developed which allow the production of any desired color (see Spirit-soluble dyes, Chapter 28). The filler will in many cases modify or influence the color; fillers are: wood flour, zinc oxide, barium sulfate, calcium sulfate, graphite, pumice, lampblack, ground asbestos, mica, and many others.

Time required for heat-hardening. In the case of the Bakelite molding compounds, the time required for molding depends upon a) the particular composition of the molding compound, b) the thickness of the piece, c) the temperature of curing, d) the type of mold. In average molding practice, with the mold at a temperature of 350° F. (177° C.), thin articles such as buttons can be molded in about 45 seconds and discharged without any cooling. Thick pieces, such as 1 inch in thickness, require 10 to 30 minutes and are cooled some time in the mold, especially if the dimensions have to be held accurately. For the average run of pieces, such as automobile distributor heads, radio tube bases, and similar ones, the time is usually between 1 and 3 minutes.

In 1935, 95,115,698 pounds of synthetic resins worth $8,730,435 dollars were produced in the United States; and of these, 52,977,234 pounds were of the phenol-formaldehyde type. Whether this supremacy will continue in future years is not certain, but likely.

(b) **Urea-formaldehyde-condensation** products representing the **amino plastics.** The urea-formaldehyde condensate is one of the products which in their final state are as clear, transparent, and colorless as glass. The others are the alkyd resins, vinyl resins, and styrene resins. The urea-formaldehyde condensate is essentially unbreakable; hitherto thick slabs have at times developed cracks on standing for six months or so. This defect has now been remedied, and the resin is proposed as a health glass substitute (Aldur, Figure 62).

One mol of urea and 3 mols of formaldehyde are heated in the presence of hexamethylenetetramine;[14] the initial condensation product is a liquid, soluble in water; on heating further, an intermediate rubber-like product is formed, insoluble in water. Continued heating, or combined

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[13] A. V. H. Mory, "Nature was suitably aided." *J. Chem. Ed.*, **6**, 817 (1929).
[14] Brit. Patent 171,094 (Fritz Pollak).

heat and pressure, yield a hard, infusible, transparent mass, insoluble in acid or alkali.

Urea and formaldehyde form mono- and dimethylol urea; it is the monomethylol urea which is probably the chief constituent of the resin. Dimethylol urea, heated alone, changes at 126° C. (258° F.) to a liquid, then at 137° C. (278° F.) to an amorphous white body which does not melt on further heating but decomposes at 260° C. (500° F.).

$$
\begin{array}{ccc}
\mathrm{NH_2 + CHOH} & \mathrm{NH.CH_2OH} & \mathrm{NH_2} \\
| & | & | \\
\mathrm{C=O} \longrightarrow & \mathrm{C=O} \;\; ; & \mathrm{C=O} \\
| & | & | \\
\mathrm{NH_2 + CHOH} & \mathrm{NH.CH_2OH} & \mathrm{NH.CH_2OH} \\
urea & dimethylol & monomethylol \\
(white\ solid) & urea & urea
\end{array}
$$
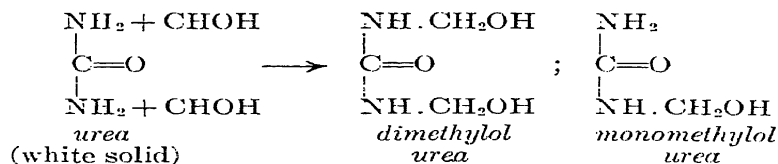
Procedure. An example of the procedure is selected, in which the evolution of gases during the hardening period is prevented, by the addition of materials which combine with formaldehyde.[15]

Six hundred parts by weight of 40 per cent formaldehyde, and 100 parts by weight of urea, are heated until 10 per cent of the whole has distilled off, leaving a product in the kettle which still contains some free formaldehyde. Enough fresh urea is added, so that there will be 1 molecule of it to every 2 molecules of free formaldehyde. After solution has taken place, the solution is evaporated further under vacuum until the mass is as viscous as possible and still allows casting into molds. The temperature is raised finally to 100° C. (212° F.).

The hardening process is completed by heating to somewhat above 80° C. (176° F.), until a hard, insoluble product forms which is fairly unaffected by water.

In the phenol-formaldehyde condensation, the water separates as an upper layer and may be most conveniently run off. In the urea-formaldehyde condensation, there comes a point when the entire mass sets, water included, and the removal of the water and subsequent washings of the resin are difficult. By changing the resin from a hydrophilic colloid to a hydrophobic one, the water is not retained with such tenacity, and its removal is comparatively simple. An example of the improved procedure follows:[16]

One hundreds parts by weight of urea, and 4000 parts by weight of 37.6 per cent formaldehyde solution are heated together in a boiler with a reflux, permitting in a short time the first condensation to take place. There is no acid present. This is the first step.

Two parts by weight of formic acid is now added, and 300 parts of thiourea, and the mix is heated further for 1 hour. Next, 2 parts by weight of alkali is added, and the mix cooled. As the cooling progresses, a white resinous product gradually separates. Two thousand

[15] U. S. Patent 1,507,624 (Fritz Pollak and Kurt Ripper).
[16] U. S. Patent 1,833,868 (Kurt Ripper).

parts by weight of water is added, kneaded into the mass, then decanted. Adhering water is removed by distillation.

The highly viscous product may be mixed with a filler and coloring matter, and then hardened.   Below 50° C. (122° F.) it does not change, but above it, the desired hardening takes place.

Instead of the thiourea, 200 parts of phenol may be added; in either case, a clear, colorless, glass-like material will be finally obtained.

On adding carbamide, there is formed the white condensation product of this substance with excess formaldehyde, and the resulting resin on being hardened yields masses similar to white milk glass.
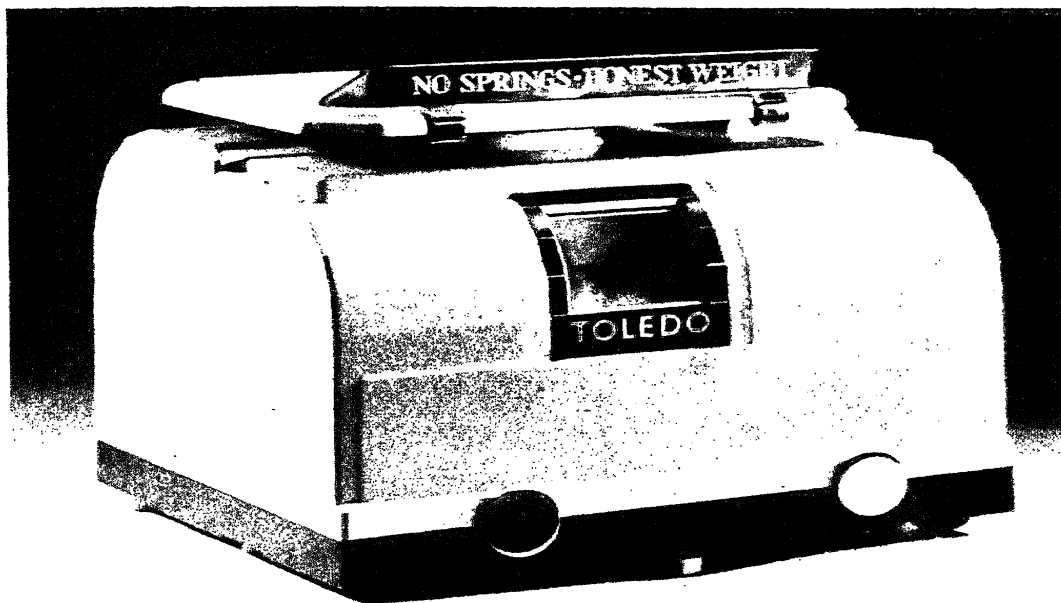
FIGURE 184.—The Plaskon Duplex Scale, to show the one-piece housing of Plaskon, a urea-formaldehyde plastic.   Kindly furnished by the Toledo Scale Company.   Width, $17\frac{3}{4}''$; depth, $15\frac{3}{4}''$; height, $15\frac{5}{8}''$.

"Plaskon" is a urea-formaldehyde molding compound, made with special care as to combining proportions, removal of unreacted components and several other cautions, so that it is successfully used as a material now standard for the manufacture of scales.   Plaskon is produced as granules or fine powder, and is used clear, or with fillers.   When first heated in the mold, it becomes plastic, then sets strong and rigid.   The molds are heated by 100-lb. steam for thin walls, by 60-lb. steam for $\frac{1}{4}$ inch walls and over.[17]

[17] "Systematic study develops new molding compound," A. M. Howald, *Chem. Met. Eng.*, **38**, 583 (1931).

The urea-formaldehyde resins were slow molding; this characteristic has been improved considerably, so that now their molding time is equivalent to that of the phenol-formaldehyde powders. The output of urea resins in 1935 was 4,202,536 pounds; the average price per pound was 46 cents.

The main outlet for urea formaldehyde-molding powders has been for toilet articles, parts for scales, drinking tumblers, and similar pieces.

Urea-furfural. Furfural (300 pounds) and urea (100 pounds) heated in the presence of a catalytic agent (4 pounds 26 per cent aqua ammonia), and a hardening agent, give a product which is convertible by heat into an infusible body.[18] With 5 per cent Chinawood oil, the final material is more flexible. This material is not of commercial importance.

(c) Thiourea-formaldehyde resins. These resins have not been manufactured in the United States since the close of 1932, because of their slow molding and the necessity for using stainless steel molds, which are more expensive.[19]

Many proposals for the production of phenol-furfural condensation products have been made (*see* item "Other Patents" at the end of the chapter), but have not become very important commercially.

(d) Phthalic anhydride-glycerin condensation products representing the alkyd resins. When 2 parts of phthalic anhydride (a white solid) and 1 part of glycerin are heated slowly at 100° C. (212° F.), there results a clear liquid. On continuing the heating to 185° C. (365° F.), there is some distillation; when this is over, the temperature is raised to 210° C. (410° F.). The first stage of the reaction is now complete. The product when cooled is a yellowish, transparent solid, soluble in acetone. The resin may also be water-white or transparent.

Heated several hours to the moderate temperature of 85° to 105° C. (185° to 221° F.), after the incorporation of filler, pigment or dye, or without these, the material is hardened to the hard infusible resin, without bubble formation.[20] A high luster is given by the contact with the mold. The type of condensation is pictured in the equations below:

$$2 \underset{\substack{phthalic \\ anhydride}}{\overset{CO}{\underset{CO}{\bigcirc}} O} + 2H_2O = 2 \underset{\substack{phthalic \\ acid}}{\overset{COOH}{\underset{COOH}{\bigcirc}}} \; ; \; 2 \overset{COOH}{\underset{COOH}{\bigcirc}} +$$

$$\underset{glycerin}{\overset{CH_2OH}{\underset{CH_2OH}{\overset{|}{\underset{|}{CHOH}}}}} = \underset{ester}{\overset{CO.O.H_2C}{\underset{CO.O.H_2C}{\bigcirc \overset{|}{\underset{|}{CHO.OC}}}}} \overset{COOH*}{\bigcirc} + 3H_2O$$

condenses further at*
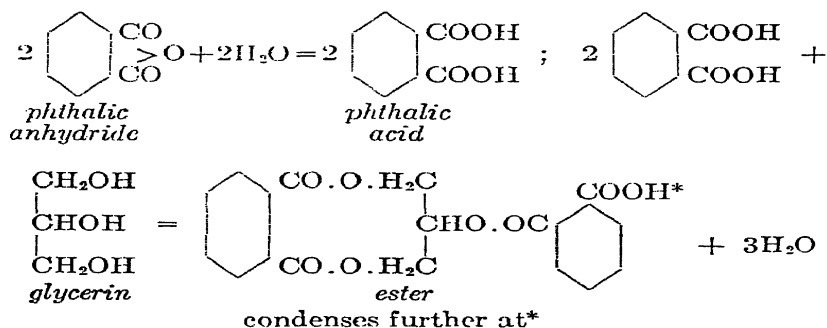
[18] U. S. Patent 1,827,824.
[19] *Chem. Met. Eng.*, **40**, 42 (1933).
[20] U. S. Patent 1,108,329.

not the exact molecular size of the resin, which is more likely to be of the order of 5000.[21]

The advantages which the molded and heat-hardened resin articles offer are: resistance to water and most chemicals, and to mechanical shocks, high dielectric value, low density, structural strength, and low heat conductivity. The plastic property of the initial material allows versatility of form. The hardened resins and the molded products may be cut, threaded, and machined.

The major use of molded products is in the manufacture of electrical insulators for the automobile, radio, telephone and airplane trade. The resins are used in increasing quantities for ornamental fittings, dials, noiseless timing gears, smokers' articles, bottle tops, fittings, clock cases, door handles, and numerous other purposes. Molded resins have become of value in chemical engineering; tanks as large as 9 feet in diameter and 10 feet high, with no reinforcement aside from an asbestos filler, have been constructed. Another example is spinning buckets for viscose silk. As molded resin does not warp, it is valuable as a frame for delicately adjusted electrical instruments, as well as for their cases.

A new and promising plastic of the phenol-formaldehyde type has recently appeared upon the market under the trade name of Haveg. As it is particularly adapted to the fabrication of chemical equipment it will be described in Chapter 45.

Laminated products consist of sheets of suitable material, such as paper, fiberboard, fabrics, coated on both sides with a solution (acetone, alcohol) of the uncured resin (resinoid A). The material is pressed, dried and then hot-pressed so that the resin sets.

Resin	Trade Strength. Members per in.
Pure phenol-formaldehyde after hardening by heat	5,000–11,000
Pure phenol-formaldehyde with a filler	6,800–12,000
Urea-formaldehyde	5,800–6,400

Motor windings and coils for auxiliary devices may be "set" in resins, particularly phenol-formaldehyde resin, itself a good insulator, by placing the coils in an autoclave filled with the fused uncured resin such

TABLE 69.—*Production and Unit Value for Synthetic Resins of Coal Tar Origin*

	Production (pounds)	Unit value	Number of producers
1927	13,452,230	$0.47	7
1928	20,411,465	0.35	9
1929	33,036,490	0.33	12
1930	30,867,752	0.30	15
1933	41,628,485	0.23	..
1934	56,059,489	0.24	..
1935	90,913,162	0.19	..

* Department of Commerce, Bureau of Foreign and Domestic Commerce.

[21] For a hard transparent resin from ethylene phthalate, 25 structural units are assumed, and a molecular weight of 4000; for a soft, transparent resin from tri-methylene phthalate, 14 structural units are accepted, molecular weight of 1700. The condensed ester as written above would probably be counted one structural unit. *Compare* W. H. Carothers, "Polymerization," *Chem. Reviews*, **8**, 365 (1931).

as resinoid A). After impregnation, the excess resin is run off, the vessel closed tight again, and the coils subjected to the heat-hardening process under pressure.

OIL-SOLUBLE SYNTHETIC RESINS

The oil-soluble resins are materials differing markedly from those discussed in the previous paragraphs, for one of the properties of molded resins is oil-insolubility. This class on the contrary must possess solution properties when added to Chinawood oil, for example, in order to be useful as film-forming constituents in varnishes. Some of the oil-soluble resins are resins for molding, modified by a subsequent treatment which introduces a dispersing agent; others owe their properties to admixtures in the original formula for making the resin, and are therefore distinct products. The more important representatives of this type of resins are given below.

Ester gum is glyceryl abietate, also called glyceryl resinate, and is made by boiling melted rosin with 11 to 12 per cent of its weight of glycerin, distilling off the water formed. The product after cooling looks very much like rosin, and has a faint odor similar to that of rosin, but it is less brittle, and its acid number is 15 and less instead of 165; this means a greater resistance to water. It has all the remarkable oil-solubilities which rosin has.

Rosin is essentially abietic acid, $C_{20}H_{30}O_2$, with which glycerin forms an ester; glycerin triresinate is the preferred form,[22] but the commercial product usually contains small amounts of di- and mono-resinates.

$$\text{Rosin} + \text{glycerin} = \text{ester gum} + \text{water}$$
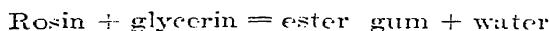
Phenol-formaldehyde resins dispersed in ester gum are available under several trade-names.[23]

Oil-soluble phenol-formaldehyde resin may be produced by modifying the phenol-formaldehyde resinoid-A by treatment with beta-naphthol or other naphthol or anthranol. For example: Phenol-formaldehyde molding resin and 30 to 50 per cent of its weight of beta-naphthol[24] are heated to 120° to 130° C. (248° to 266° F.) in a still; water is distilled off. Spontaneous heating causes a rise to 145° C. (293° F.) at which point it is held for $1\frac{1}{2}$ hours. On being run off and cooled, a translucent, brittle mass is obtained which dissolves in varnish oils.

The resin so made cannot be heat-hardened, but if catalyzing agents (metal resinates) are added in the course of the preparation, the resulting resin may be hardened.

In modifications of the procedure, 2 to 10 per cent (on the weight of the mass) of linseed oil, and 5 to 10 per cent of mild oxidizing agents

[22] *Paint Varnish Prod. Mgr.*, **8**, Dec., 1932, sect. 1, p. 5.

[23] Such as Amberol, Beckesite; but it should be remembered that the trade name does not establish the exact nature of a product; under the same name, several products may be made.

[24] U. S. Patent 1,809,732, the Seebach patent. Using the trade names, the Bakelite series is represented by Oil-soluble Bakelite XR 254 [*Ind. Eng. Chem.*, **22**, 1182 (1930)], and others.

such as nitronaphthol may be added. Air or nitrous fumes may be passed through the melt.

Glycerin and phthalic anhydride condensed in the presence of the fatty acids from linseed oil yield oil-soluble resins, such as "modified glyptal", which have proved very satisfactory. "Oil-soluble Rezyl" is another well-known representative of this class, and contains fatty acids, or rosin, or both. "Oil-soluble Teglac" is a glycerin-phthalic anhydride condensate modified by rosin principally.

The oil-soluble alkyd resins[25] are a group of resins including among others an ethylene glycol-phthalic anhydride condensate modified by unsaturated fatty acids from a drying oil. In general the oil-soluble alkyd resins for varnish making may be said to be esters of polybasic acids and polyhydric alcohols, modified by unsaturated fatty acids such as oleic acid, or by oils of the drying type.

In process of development are resins produced from unsaturated petroleum hydrocarbons (the di-enes), polymerized by the action of aluminum chloride. Such resins do not yellow, and are on the acid side; at present, rosin is generally incorporated. For a high yield of resin a highly unsaturated distillate rich in diolefins and olefins[26] is best suited; a number of reactions take place simultaneously. The one leading to resins is controlled in part by the amount of catalyst, namely 2 per cent, and is favored by the presence of the proper ratio of diolefins and olefins,[27] which undergo a polymerization. Olefins alone lead rather to synthetic lubricating oils.[28]

Polymerized Resins;[28a] Vinyl Resins. Vinyl chloride $CH_2.CHCl$ (Chapter 25) may be polymerized by ultra-violet light and by other agencies to a thermoplastic resin (Vinylite). In blocks, it is water-white, and transparent to ultra-violet light; powdered, it forms a white powder, whose solution in acetone and other ketone solvents serves as a varnish. The value of the vinyl resins is mainly as molding material; a low temperature coefficient allows the manufacture of panels and large pieces. It takes dyes readily, and may be shaped in the mold and under heat.

Polymerized Hydrocarbon Resins. The most important of these is the para-coumarone-indene resin sold under the trade name of Cumar. It is manufactured from coal-tar naphtha recovered at by-product coke ovens or through tar distillation. The naphtha utilized has a boiling range of 150° to 200° C. and contains coumarone and indene.

The naphtha is treated with sulfuric acid in the cold, polymerizing the active ingredients to form the resin. The unreacted portion of the

[25] *Chem. Met. Eng.*, **39**, 599 (1932).

[26] Ethylene CH_2: CH_2 is the simplest olefin; a diolefin has two double bonds; there are cyclic olefins as well as non-cyclic ones.

[27] *Ind. Eng. Chem.* **24**, 1125 (1932).

[28] *Ind. Eng. Chem.*, **23**, 604 (1931).

[28a] Ideal conditions for polymerization are: 1) the double bond; 2) the conjugated double bond; 3) unsymmetrical arrangement; 4) formation of mixtures; 5) position isomers; 6) variable reaction trends; 7) multiple functional groups; 8) formation of long chains; 9) associate linkage; 10) state of aggregation. Further, consider the unsaturation, or double bond; in the double bonded grouping, substituting hydrogen by negative groups enhances the polymerizing power; but only up to a certain point; too much negativity inhibits polymerization. Finally, in general, the more highly polymerized the molecule, the harder the resin.

CH
‖
CH
O
coumarone
(liquid)

CH
|
CH
CH₂
indene
(liquid)
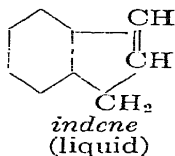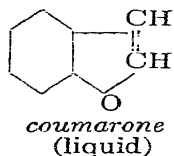
polymerize to form solid resins.

naphtha is removed by distillation. The resin remaining in the still cools to a light brown, brittle, odorless solid, soluble in oils and organic solvents. It is a neutral resin, alkali- and acid-resisting and with good electrical resistance. The melting range for the purest grade is 150° to 160° C. (300° to 320° F.). Other grades melt as low as 5° to 15° C. (40° to 59° F.). It is used in the varnish, waterproofing, rubber, printing ink, flooring and adhesive industries.

Styrene $C_6H_5.CH:CH_2$ (a modified ethylene), a liquid, is polymerized to a resin on heating and is now available as a molding powder.

Polymerized methyl α-methyl acrylate has already established itself in the manufacture of laminated glass[28b]; it is formed also in blocks, rods. and tubes under the name of Lucite.
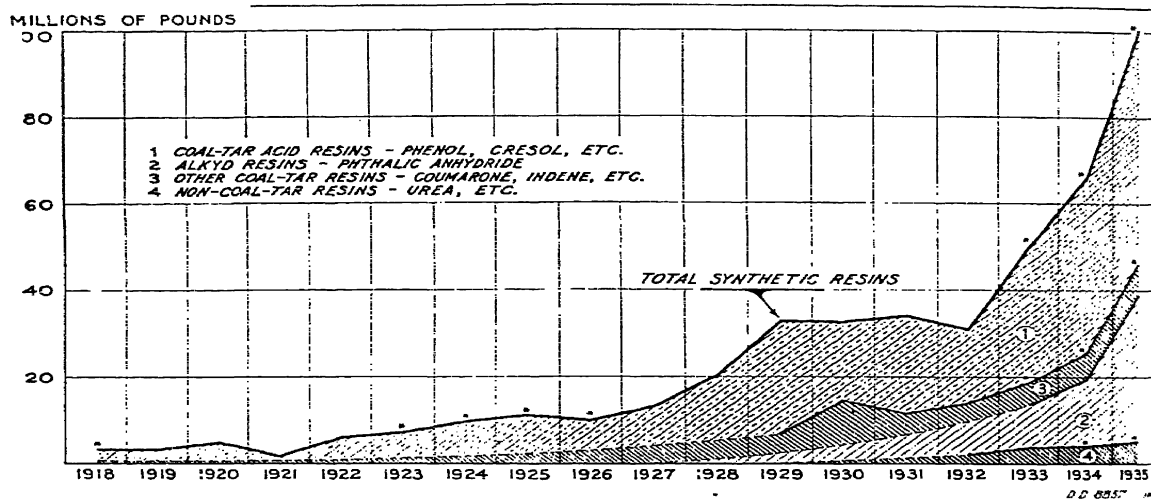
FIGURE 185.—The production of synthetic resins over a period of years in the United States. (From "Survey of current business," Bureau of Foreign and Domestic Commerce, under title, "Plastics-Products of Ever-widening Utility.")

Butadiene like isoprene polymerizes to rubber or rubber-like substances; 2-chlor-1,3, butadiene produces Neoprene (Chapter 39).

Aroclors are chlorinated biphenyls, sold in the form of thick oils or resin-like solids, whose chief use is in lacquers. The nitrocellulose film

[28b] *See* Chapter 11, and U. S. Patent 2,032,663.
On polymerizing acrylic acid and esters, 2,008,719 and 2,014,923.

containing an aroclor is more nearly fireproof, and also more brilliant. The aroclors are not oil-soluble.

Halowax is a chlorinated naphthalene produced either in the form of a wax or an oil. The wax is used as condenser impregnation; in moisture-, and flame-, acid-and insect proofing wood and fabrics and in moisture- and flame-proofing wire and cable. The oil is a good solvent for rubber and can be mixed with asphalt, wax, pitch, etc. It is used as a lubricant and plasticizer and as a standard for testing index of refraction.

Mowilith, a recent addition to the long list of synthetic resins and resin-like products is produced in two steps. Monochloracetic acid and acetylene react with mercuric sulfate as a catalyst, at 70° C. (158° F.), followed by further condensation under the influence of ultra-violet light. It is soluble in the lacquer solvents.

SYNTHETIC PHENOL

Natural phenol is phenol obtained in the distillation of coal-tar[29] and to a smaller extent in the purification of ammonia liquors in coke- and gas plants.[29] Synthetic phenol is phenol made from benzene, either by sulfonation followed by alkaline fusion, or by chlorination and subsequent heating under pressure with caustic soda solution; it is in reality a semi-synthetic.

Natural phenol is by no means unimportant. The estimated United States production of tar for 1929 was 700 million gallons; its phenol content averages 0.7 per cent, so that 50 million pounds of phenol were available. Only 13 million were extracted, the rest was lost in the burning of the crude tar for fuel, in open hearth steel furnaces, for example. The explanation is that the extraction of phenol from its tar fraction requires a special plant and staff, and a market must be found for a number of other products extracted. Unless the price for phenol is very attractive, it is not worth while to undertake the operation.

Synthetic phenol was manufactured to meet the war emergency; in 1918, 107 million pounds were produced. In the next two years, plants were dismantled, as it was expected that the normal production of natural phenol would suffice. No synthetic phenol was manufactured in 1921. The phenol formaldehyde resins appeared on the market in 1922 and 1923, and created a large demand for phenol, which led to the installation of several plants. In 1924, the production was 10 million pounds, mainly synthetic (30 cents a pound). In 1929, 24 millions were produced by all methods (11 cents); in 1930, the total production was 21 millions (11 cents), while in 1935, it was 43,418,579 pounds, with value of 10 cents a pound. About one-half was synthetic, with the two processes about equal. Many millions of pounds are produced by the chlorphenol method, which is simpler than the sulfonation method; only by introducing several improvements did one or two exceptionally well equipped plants maintain production by the latter method.

[29] Chapter 14.

Benzene Sulfonate Method. In the early developments, benzene C_6H_6 was treated with oleum,[30] the benzene sulfonate $C_6H_5.SO_3H$ was isolated by neutralizing both excess acid and sulfonate with lime, and filtering the calcium sulfate from the solution of calcium benzene sulfonate. An improvement was made when the continuous sulfonation method of Dennis and Bull was installed.[31] Four sulfonating tanks are used in series, and in each, the benzene enters at the base through perforated pipes, so that it rises in the form of fine droplets. The sulfonated benzene remains dissolved in the great excess of benzene which is provided. The benzene flows countercurrent to the acid; the latter is 98 per cent H_2SO_4 at the entry to the first tank, 77 per cent at the exit of the fourth, when its sulfonating power is exhausted. It is concentrated to 93 per cent and new oleum is added to it, to reach the required 98 per cent strength. The benzene with 2 per cent sulfonate is washed with water (3 washers), the sulfonate in the water solution neutralized with sodium sulfite recovered from the last step in the process, and concentrated.

$$2C_6H_5.SO_3H+Na_2SO_3=2C_6H_5.SO_3Na+SO_2+H_2O.$$
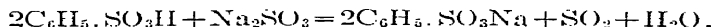
The strong solution of sodium benzene sulfonate is run, gradually, into fused caustic soda at 320° to 350° C. (608° to 662° F.); sodium phenolate and sodium sulfite are formed.

$$C_6H_5.SO_3Na+2NaOH=C_6H_5.ONa+Na_2SO_3+H_2O.$$

The melt is dissolved in a limited amount of water, sufficient to dissolve the sodium phenolate only; the sodium sulfite remains as a wet solid, which after washing and drying, serves for the neutralization of new amounts of benzene sulfonate. Only half the sulfite produced is needed in this way; the other half may be sold (by-product).

The sodium phenolate in solution is decomposed by carbon dioxide from a lime kiln; phenol and sodium carbonate are formed. The latter

$$2C_6H_5.ONa+H_2O+CO_2=2C_6H_5.OH+Na_2CO_3.$$
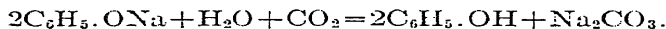
is causticized by lime from the kiln. To complete the reaction, a small amount of nitre cake is added. The phenol separates as an upper layer; it is run off and distilled from a pot still.

Chlorbenzene Method. For many years attempts were made to produce phenol commercially from chlorbenzene, without result. It remained for an American firm to discover the proper apparatus, reaction mix and operating conditions which have made the process a commercial success. Starting with chlorbenzene, the method as practiced is as follows: [32, 33]

Chlorbenzene (1 mol) is emulsified with a 10 per cent aqueous caustic soda solution ($1\frac{1}{4}$ mol) and the emulsion (oil droplets in water) pumped

[30] Chapter 27.
[31] *Ind. Eng. Chem.*, **10**, 738 (1918).
[32] *Ind. Eng. Chem.*, **20**, 114 (1928).
[33] U. S. Patent 1,607,618.

under a pressure of 200 atmospheres into a multitubular reaction vessel, with recirculation, and continuous discharge of a small portion, which is just made up by the entering emulsion. The liquid travels through the tubes with a sufficient turbulence to maintain the dispersion of the chlorbenzene. The tubes are made of copper, in several units 1½ inch outside diameter, with thick walls; a temperature of 320° C. (608° F.) is maintained by means of diphenyl oxide vapor under moderate pressure. The copper wall acts as a catalyst. As the phenol forms, it dissolves in the water, so that the remaining chlorbenzene is not diluted by it. The conversion is nearly 100, if the circulation period allows any one part of the charge to remain within the tubular vessel for 30 minutes. The reaction is:

$$C_6H_5Cl + 2NaOH = C_6H_5ONa + NaCl; \quad C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$$
chloro-
benzene   *phenol*
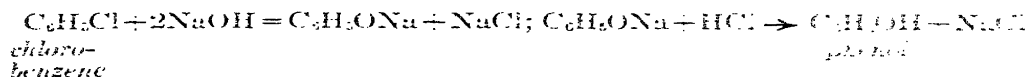
On leaving the reaction vessel, the liquid passes through the exchanger to heat the incoming liquids, then through coolers, after which the pressure is released. The free phenol is formed by a treatment with acid, giving two layers. The upper layer is run off and distilled in a chromium-plated still [34]; some water passes over first, next any unchanged chlorbenzene, near 132° C. (270° F.), then the phenol, near 181° C. (358° F.), while diphenyl oxide remains in the still. The latter's boiling point is 259° C. (498° F.). The recovery of phenol is nearly the theoretical one.

An attempt has been made to hydrolyze benzene sulfonic acid with aqueous caustic,[35] under pressure and at elevated temperatures, as in the chlorbenzene method.

It has been proposed to make phenol from benzene by sulfur trioxide action in liquid sulfur dioxide.[35a]

Uses. The main consumption for phenol is the synthetic resin industry. A sizeable quantity serves as disinfectant and preservative, while about 4 million pounds a year are the starting material for the manufacture of pharmaceuticals, such as salicylic acid and derivatives, and dye intermediates.

FORMALDEHYDE

Formaldehyde, CHOH, is a gas which is very soluble in water; it is this strong solution which enters the market. Formaldehyde is made by the partial oxidation of methyl alcohol catalyzed by copper gauze, the contact agent very generally employed, or other agents. A mixture of air and alcohol is necessary, and is provided by bubbling air through warm methyl alcohol placed in a copper vessel fitted with steam coils. The air-alcohol mixture passes a dephlegmator held at 40° to 50° C.

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[34] U. S. Patent 1,824,867
[35] U. S. Patent 1,789,071.
[35a] U. S. Patent 2,007,327.

(104° to 122° F.) and then enters the converter. This vessel contains a number of copper tubes in which rolled copper gauze in form of plugs is placed throughout their length, usually with a glass lining, for easy removal. In the installations with copper gauze, the temperature maintains itself at 550° to 600° C. (1022° to 1112° F.) by the heat liberated during the reaction. The gases leaving the converter contain formaldehyde, some methyl alcohol, hydrogen, nitrogen and water. They must be cooled suddenly in order to prevent side reactions; this is accomplished by passing them at once to an absorber, where a cool hydrous solution meets them, and at the same time abstracts the formaldehyde. There is formed a water solution containing 30, 35, or 40 per cent CHOH by weight, and some methyl alcohol, esters and methylal. In a second absorption vessel, methyl alcohol is retained. The outgoing gases are scrubbed for small amounts of alcohol, the weak solution concentrated in a column still, and the recovered material used in the process. The crude formaldehyde may be refined by a distillation.

Operating as just described, the yield lay between 60 and 65 per cent. It was found that by maintaining the reaction mixture neutral, the formation of by-products is decreased, and the yield correspondingly raised. The neutrality is insured by feeding a small amount of ammonia to the entering gas mixture.[36]

The explanation of the reaction is that, first, the methyl alcohol molecule is dehydrogenated by the metal. Next, oxide formation by the metal takes place, and this is the function of the air. The oxide reacts with the hydrogen, removing it from the system, thus allowing the dehydrogenation to proceed further. The water formed leaves with the formaldehyde. The net reaction is $2CH_3OH + O_2 = 2CHOH + 2H_2O$.

A catalyst consisting of iron and molybdenum oxide has been found to be very effective; the molybdenum possesses directive power, while the iron has a high activity for conversion. A lower temperature is sufficient.

To copper, and other metallic catalysts, two substances are poisons in the formaldehyde reaction; they are acetone and water. For this reason, synthetic methanol, furnished free of acetone as well as anhydrous, is to be preferred to wood alcohol. With vanadium pentoxide as the catalyst, however, methyl alcohol with as high as 5 per cent acetone may be used, without loss of efficiency. The temperature, moreover, is only 225° C. (437° F.)[37]; in all cases, the lower the temperature, the higher the yield.

It would seem simpler to hydrogenate carbon monoxide to formaldehyde $CO + H_2 = CHOH$ instead of oxidizing methanol, which itself is made, at least in large part, by hydrogenating carbon monoxide. And indeed, several proposals have been made which embody this principle. In one of them,[38] water gas made from wood charcoal is passed over a

[36] U. S. Patent 1,738,745, quoted through Marek and Hahn, "The catalytic oxidation of organic compounds in the vapor phase," New York, Chemical Catalog Co., Inc., 1932, p. 145.
[37] U. S. Patent 1,383,059.
[38] U. S. Patent 1,824,896.

catalyst at 200° to 300° C. (392° to 572° F.) under a pressure of 10 atmospheres. The catalyst consists of the oxidizing agents vanadium pentoxide and chromium oxide and diatomaceous earth, with smaller amounts of silver, zinc, cadmium and platinum deposited from their salts. Rapid cooling of the gases leaving the converter, with a water spray, for example, gives a good yield of formaldehyde. The process allows as an alternative the passing of the formaldehyde vapors with more hydrogen to another catalyst in which the mild reducers predominate, there to form methanol.

The reaction $CO + H_2 = CHOH - 0.7$ Cal. is slightly endothermic; while $CHOH + H_2 = CH_3OH + 27.9$ Cal is strongly exothermic.

Natural gas has been made the source for the direct production of formaldehyde (and methyl alcohol).[39]

Formaldehyde as a by-product is obtained by the natural gas companies incidental to the removal of oxygen from the gas, in order to lessen corrosion. The materials removed in the process consist of formaldehyde, methyl alcohol, and other aldehyde. This source may become commercially important.

Formaldehyde is extremely reactive; its uses are correspondingly numerous. It serves as an insecticide and disinfectant (Chapter 38), as a chemical reagent in synthesizing organic compounds, as an embalming fluid, as a hardening agent for casein; its most important use from the standpoint of tonnage is for the manufacture of synthetic resins.

The yearly production of formaldehyde solution is 50 million pounds, valued at 6 cents a pound.

Other raw materials for synthetic resins will be found under the proper heading, or by consulting the index.

PYROXYLIN PLASTICS

Pyroxylin contains nitrated cellulose, with 11 to 12 per cent nitrogen, while gun-cotton contains more highly nitrated cellulose, with more than 12.5 per cent nitrogen. The manufacture of pyroxylin and its use in lacquers are presented in Chapter 31; it is pyroxylin as a plastic which is of interest in the present discussion. For this purpose, camphor and castor oil, for example, are worked in, giving flexible pyroxylin sheets. A well-known pyroxylin plastic is Celluloid; other trade names are Fiberloid, Viscoloid, Leatheroid, Pyralin.

Celluloid [40] is a solid which softens at 75° C., so that at that temperature it may be pressed, twisted, shaped in many ways, to forms which after cooling are persistent. It consists of nitrocellulose (2 parts) and camphor (1 part), with one or several other substances added to stabilize it and give color. An early formula was:

[39] Brit. Patent 295,356 (Aug., 1927), by the Empire Gas, Oil and Refining Co., Okmulgee, Oklahoma.

[40] The name was coined by the Hyatt brothers; John Wesley Hyatt took out many patents, for example U. S. Patent 88,633 in 1869. In that day, the development of the new plastic was a greater sensation than that of the synthetic resins have been in the past decade.

	Parts by wt
Camphor or camphor oil	20
Castor or linseed oil	40
Nitrocellulose or "xylodine"	40

The method of preparation consists of mixing the water-wet nitrocellulose with powdered camphor, sprinkling alcohol on the mix, and kneading at a low temperature for several hours. At this lower temperature (35° C.) the operation is safer than at the higher temperature necessary for drier materials. The resulting mass is soft, and by heat and pressure it is formed into sheets, blocks, and other shapes.

Pigments are incorporated during the kneading; zinc white for example gives a white resembling ivory. For transparent plastics, urea is added as stabilizer (antacid); in the white Celluloid, the zinc oxide is both pigment and stabilizer.

There is another method practiced chiefly in Europe, in which an alcoholic solution of camphor is allowed to stand over pyroxylin, and after some time all are mixed under heated rolls; the solvents are recovered. The soft mass is shaped as stated above.

Camphor not only plasticizes pyroxylin, but robs it of its explosive property; the plastic remains flammable, however, but hardly more so than any other combustible material. The shaped articles must be allowed to season in closets at 30° C., until all solvents have evaporated.

A special kind of pyroxylin plastic is used for the manufacture of moving picture films; the camphor for this purpose is usually purified by solution in alcohol and filtration; the formula specifies a higher proportion of pyroxylin which is dissolved in methanol, amyl acetate, and other combinations of solvents, to produce at once a thick solution low in camphor (3 per cent). This solution is fed to a large cast-iron wheel (15 feet in diameter and larger), perfectly balanced, with its 18-inch face silvered and polished; the wheel turns slowly, so that the liquid fed in at one place dries sufficiently to permit removal before a whole revolution has been made. The film is continuous, and wide enough to give a number of strips of the standard size (32 mm. wide) for moving-picture cameras. The film base, after suitable drying, is coated with the gelatin carrying the silver salts.[41] It is not plastic, but it is flexible.

There are a number of other formulas for pyroxylin plastic films for moving pictures. In addition cellulose acetate film, which is not flammable, has been introduced. Following fatal explosions traced to stored X-ray films of pyroxylin, tests were made [42] with cellulose acetate films, which showed them to be essentially unaffected by the temperatures and length of heating which produced explosions and toxic gases with the pyroxylin films.

In order to reduce the flammability of pyroxylin plastics, denitration has not proved satisfactory, as it interferes with the plasticity of the

[41] Chapter 37.
[42] "Jahresbericht VII der Chemisch-Technischen Reichsanstalt," Berlin, Verlag Chemie, 1928. pp. 90-111.

material. Salts such as magnesium chloride have been added, with more success. As a rule, nothing is added. (Compare p. 604.)

Pyroxylin solutions are used as dips for gas mantles and for other purposes.

A considerable market has been opened to pyroxylin plastics by the invention of laminated glass for safety glass (Chapter 11).

ACETO-CELLULOSE PLASTICS

Pressing the pyroxylin plastic are the plastics made from cellulose acetate, in which plasticizers, solvents and softeners are incorporated to produce a plastic, highly transparent to light waves. Photographic films and moving picture films may now be obtained either on cellulose acetate plastic, or on nitrocellulose plastic. The acetate cellulose plastic is not markedly flammable; it is a "safety film." In 1935, there were produced 10,504,003 pounds of cellulose acetate plastic, and 16,245,313 pounds of nitrocellulose or pyroxylin plastics. Aceto-cellulose plastic is used as a lacquer and coating, as well as in sheet, rod and tube form.

Camphor. Natural camphor is obtained from the camphor tree, *Laurus camphora*, which grows in Japan and in Formosa. The tree, preferably 50 years old, is chopped small, and boiled with water at a slow rate; the escaping steam carries the camphor away to the condenser, where the camphor forms a crust on the condensed water. The crude material obtained is pressed free of the greater part of the camphor oil, and purified further by sublimation.

Besides the natural camphor, synthetic camphor is available. It is made, in one method, by heating anhydrous turpentine (5 parts) and oxalic acid (1 part) to 120° C. (248° F.); the material obtained by steam distilling consists of borneol $C_{10}H_{17}OH$ (an alcohol) and camphor $C_{10}H_{16}O$. A treatment with sodium bichromate and sulfuric acid changes the borneol into camphor. Synthetic camphor is made in the United States at the rate of many tons a day.

Statistics are given in Table 70 for the three grades of camphor imported, crude and refined natural camphor, and synthetic camphor.

TABLE 70.—*Camphor Importations, 1935.*

	Pounds	Value	Cents per pound
Crude natural camphor	1,541,936	$422,133	27
Refined	1,256,278	499,356	40
Synthetic	925,896	321,021	35

Instead of camphor, other substances have been successfully used as plasticizers for pyroxylin, particularly tricresyl phosphate, a liquid, and triphenyl phosphate, somewhat dearer, a solid. They are made by heating cresol or phenol with phosphorus trichloride in the presence of aluminum chloride.

CASEIN

Still another plastic is casein plastic, of which Galalith is an example. The raw material is casein, the white curds which separate from skim milk on addition of lactic or acetic acid, or of rennet, an enzyme obtained from the calf's stomach lining. The rennet casein is higher in ash content (7 per cent) than the acid-precipitated casein, and is preferred for the manufacture of the plastic. After precipitating the casein, there is left in the milk liquor milk sugar and albumin, which may be recovered. Much of the casein is imported, in the form of dry granules.

In order to prepare the plastic, the casein is powdered, mixed with a coloring matter or a filler, moistened with enough hot water to form a dough, which is then passed between heated rolls to form sheets. A number of sheets may be pressed to a block or other shape, while rods and tubes are made directly by means of an extrusion machine. The shaped pieces are placed in a solution of formaldehyde, which "sets" them, that is, renders them as hard as stone; finally they are dried in a warm closet.

The most important outlet for these hardened sheets is for the button trade. Very beautiful results may be produced by incorporating a pigment in the original mass, shaping the button. dyeing it on the surface. cutting a design which exposes the body color, contrasting with the surface color.

Casein is used for many other purposes, for example as a glue and for sizing paper.

Vulcanized fiber is presented in Chapter 22, under cellulose.

The relative value as insulators [43] for some of the substances described in this chapter, with some common substances for comparison, is shown below. In the choice of an insulator, such other qualities as resistance to heat and mechanical strength must be considered.

	Puncturing Voltage per Millimeter of Thickness
Fiber red	2,000 to 10,000
Phenol resins	2,550
Hardened casein plastic	6,000
Glass (common)	8,000
Celluloid	15,000
Hard rubber	15,000 to 38,000
Mica	28,000

Plioform. A new type of plastic is made from rubber and sold under the trade name Plioform. It requires no vulcanization. It offers the acid and alkali resistance of rubber and is tasteless and odorless. It is produced in all colors, in translucent and transparent form.

OTHER PATENTS

U. S. Patent 1,946,040, catalyst for the nuclear chlorination of benzene compounds and using same; 2,068,926, method of making artificial lumber by incorporating synthetic resin forming ingredients, such as urea and formaldehyde;

[43] In part from "Marks' mechanical engineering handbook," McGraw-Hill Book Co., 1916, p. 1597.

2,069,183, on a Halowax; 2,069,178, method of dispersing resins and composition produced thereby; 1,793,310-2, on making synthetic resins; 1,820,816, a cheap resin from phenol and glucose; 7,753,630, a cheap resin from starch; 1,619,692, glyptal in their composition for commutators; 1,619,758, glyptal with mica flakes; additional, 1,589,094; 1,806,798, process for making phenolic compounds in circulatory tubular systems; 1,851,754, manufacture of formaldehyde by passing methanol and air in contact with vanadium oxide and a combustion retarder; 1,744,265, formaldehyde from methanol; Brit. Pat. 344,796, iron carbonyl removal from the methanol insures longer life to the silver gauze catalyst. For phenol-furfural condensation products: 1,705,493; 1,898,146; 1,592,773; 1,705,493; 1,705,494.

PROBLEMS

1. Taking the procedure for the phenol-formaldehyde resin, for the varnish that is given in the text, what will be the weight of the product finished resin if the yield is 88 per cent and nothing is lost except the water of reaction and of which is in the formaldehyde? 1000 lbs. of phenol are taken.

2. A shipment of 2500 lbs. of ester gum is made. If the ester is pure glycerin glycerin triresinate, how much glycerin and how much rosin were required? The glycerin is 98 per cent, and the rosin 95 per cent obtainable.

3. It is required to make 1000 pounds of phenol from chlorbenzene. Let the conversion be 100 per cent, how much chlorbenzene is needed? In the manufacture of chlorobenzene, the chlorination of benzene leads to a 90 per cent recovery, how much chlorine in pounds and benzene in gallons are called for? The density of benzene is 0.879. In the recovery of the hydrochloric acid, if is found that only 90 per cent of the amount evolved is absorbed, the rest is lost, how many gallons of 22° Bé. acid will be collected? Answers: 125.7 gallons benzene; 883.3 lbs. 22° Bé. acid.

4. To make 1000 gallons of formaldehyde solution of 40 per cent CH_2O by weight with density 1.128, from methanol by air oxidation, how much methanol in pounds is necessary, if the yield is 60 per cent? The methanol is made by the synthesis of CO and H_2, which gives a recovery of 100 per cent; what weight of CO and of H_2 is required to make the required amount of methanol? Answers: 7863 lbs. CO and 883.3 lbs. H_2. To make the same 1000 gallons of formaldehyde also directly from carbon monoxide and hydrogen, what weight of hydrogen and of carbon monoxide would be needed if the recovery is (a) 60 per cent; (b) 80 per cent?

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The history of tanning reaches almost as far back as the history of man: compared with it, the science of chemistry is indeed young. Yet in the past fifty years, chemistry has furnished the tanner a new method, chrome tanning. In the older vegetable tanning, chemistry has simplified the process, furnished a partial explanation of the reactions, a variety of tanning agents, and methods for testing them and for recording the steps in the manufacture. With the aid of the chemical engineer, the time required for the vegetable tanning process has been shortened.

Chapter 36

Leather, Gelatin, and Glue*

Leather is the skin of animals, cleaned, and treated with oil, grease, or astringent vegetable matters which arrest its decay and make it more or less pliant. Before tanning, a skin can be dissolved in warm water; after tanning, it is insoluble. The fresh skin heated in water dissolves and gives a solution of gelatin, which on cooling solidifies; if tannin be added to the warm solution, the gelatin is precipitated. Glue is gelatin which has been heated longer in the water; it jells less readily, but is more sticky.

The skins of bulls, cows, oxen, heifers, and calves are naturally used for the larger sizes; the last three give the more uniform and thinner leather. The skins of sheep and goats, to a lesser extent those of the kangaroo and certain species of seals, are used for the smaller sizes; they give the softer leathers for shoe uppers and gloves. The skin of the horse and the pony is also made into leather, but is of small importance.

With unimportant exceptions, skins may be said to be by-products of the meat industry; the animal is raised, and later killed for its meat, and incidentally, its skin is saved and sold to the tanner. If skins were a primary product, leather would be much dearer. This circumstance carries with it also certain penalties, in that the rancher for instance damages the best part of the skins by branding, is less careful about insects which perforate the skin, and is at times careless in the removal (flaying) of the skin and in its curing.

The skin has an upper thin layer, the epidermis, which carries in a small depression the hair follicle and the hair itself. Below this is the derma, or corium, many times thicker than the epidermis; it is the true leather-forming substance. Making leather means removing the hair and the epidermis, cleaning the flesh side from the under skin, and treating the corium so that it will no longer be susceptible to bacterial decay. The corium has a fibrous structure; untreated, it will absorb water as gelatin does; in fact it is at least 85 per cent collagen, on a dry basis, and collagen with water forms gelatin; the tanning process renders the corium

* Gelatin and glue in collaboration with Mr. H. F. Lichtenberg, consulting chemist and bacteriologist for food and dairy products, Buffalo, N. Y.

fibers water-resisting, within limits. Skins are not uniform in thickness throughout their area; the thickest part is at the butt.

The skins of the seal, walrus, and porpoise have been made into a leather for many years; within the last 15 years, the skin of the shark and the ray has been utilized in making leather. The shark carries a calcareous coating over the skin, known as shagreen; this is removed; from there on the tanning is similar to that for cow hide.

Two main divisions in tanning are observed, chrome tanning and vegetable tanning. Chrome tanning is more modern and requires less time; it is used for the smaller skins, the "kips" and "skins"[2] of the tanner, which are made into shoe uppers. Vegetable tanning is used for sole leather and leather belting, also for the smaller skins to a certain extent; it is a longer process, four months would be rapid. In chrome tanning, five to six weeks from the hide house to the warehouse is customary.

Preliminary Treatment of the Skins. The skins are received in the hide house in various conditions. Fresh skins from nearby slaughterhouses have received a treatment with salt, rubbed on the flesh side; skins from South America are sun-dried, as stiff as boards. The bundles of fresh salted skins are opened, each one examined for defects, and the ends which would not make leather, such as ears and hoofs, are cut off and sent to the gelatin or glue maker. They are then scoured to remove salt and dirt. The dried skins[3] are soaked longer to restore them as near as possible to their original condition.

Liming is next; it is done in pits flush with the floor. Hides require 7 to 10 days to pass the pits, of which there are usually three; while in the pit, the hides are occasionally handled. The effect of liming is: *a*, to loosen the hair and epidermis; *b*, to swell the corium, which results from a division of the coarser fibers into its constituent fibrils; *c*, to emulsify or saponify the grease normally present in the corium. This effect is due partly to the alkalinity maintained by the excess of lime, partly to its hydrolytic action, and partly to bacterial action. The liming for the kips and skins requires less time, 1 to 3 days. Sodium sulfide, Na_2S, is sometimes added to the lime suspension, as it acts much faster; or sodium sulfide mixed with lime and water to a thin paste is painted on the hair side of the skins, these then folded hair sides together, and piled on the floor over night; the next morning, the hair is loosened. For certain sheep hides with valuable wool, the paste is painted on the flesh side, folded flesh sides together, left piled over night, and the next day the wool can be pulled out as if it merely lay there.

The hide or skin is then ready to be scraped (beam-house work), formerly by hand, over a beam; now in a machine with spiral knives which rotate fast against the skin which is moved in slowly. On the

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[1] U. S. Patent 1,338,531.

[2] Hides are 25 sq. ft. in area; kips between 25 and 15 sq. ft.; skins less than 15 sq. ft.

[3] Such dried hide or rawhide is durable; for instance the tabernacle of the Latter-day Saints at Salt Lake City was constructed with rawhide strips instead of nails in 1850 and is still in daily use.

hair side the hair and epidermis are removed; on the flesh side any adhering particle of flesh and the under-skin. The hides are cut into butt, shoulder and belly pieces, or merely in two; they are not cut if the leather is to make belting for machinery, for which as large a surface as possible is desired. The skins are next delimed in the baths (with ammonium salts), or in an acid bath, containing lactic, acetic, or formic acid.

Vegetable Tanning, Sole Leather and Belting. After deliming and washing, the hides, now called pelts, are ready for tanning. They are suspended from a wooden stick in a nearly spent tanning liquor and moved up and down a short distance by a mechanical rocker; after one or two days, the pelts are moved to a second pit, containing somewhat stronger liquor, where the rocking is by hand and less frequent. The pelts are moved to a still stronger pit, always suspended until they are ready for the strongest tanning liquors. These are applied to the pelts laid horizontally in a pit, with crushed tan bark laid on top of each; when all the pelts are in, the liquor is run in to fill the pit. The pelts remain in such liquors for periods of two, three, or more months, with several repackings. Tannin is absorbed, and adds to the weight of the leather. The period has been shortened by placing pelts, liquor, and bark in a wooden drum and rotating it.

On removal from these pits, which are called "layaways", the leather is washed in warm water, the wrinkles smoothed out, and oiled. Now it is stuffed with oil or grease, either by hand or by machinery. Sole leather receives only 2 per cent grease; belting leather 8 to 10 per cent; harness leather 20 to 25 per cent.

The tanning materials vary in tannin content from 3 per cent in chestnut wood to 30 per cent in the dried myrobalan fruit. The earliest tanning agents were hemlock bark or oak bark; as the forest receded the tanners moved from the modest original settlement on Manhattan Island in two general directions. The tanners using oak bark moved into Pennsylvania, Virginia, West Virginia, North Carolina, and Tennessee. The tanners who used hemlock bark moved to lower New York State, Pennsylvania, Michigan, and northern Wisconsin. Other areas have been added; in the Southern States chestnut wood has become an important tanning agent. In addition to the tanning materials proper, extracts are made and shipped long distances.[4] This has been all the more welcome as otherwise the tanner must make his own extracts. Chestnut wood extract is a liquid and contains 30 per cent tannin. Oak bark and hemlock bark each contain 11 to 13 per cent tannins; mimosa bark from India contains 30 per cent. The quebracho tree of South America has 20 per cent in its wood; an extract is made which contains 60 per cent, a solid. The materials listed in this paragraph belong to the catechol tannins; on heating them, the parent substance

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[3a] *See* under chrome tanning.

[4] The spent wood chips have been utilized as a source of cellulose for paper and similar products, or, as in the Bergius process (Chapter 16), for hydrolysis to sugars.

catechol, 1,2-dihydroxybenzene, is obtained; with iron salts, they give a green-black coloration.

Another group of tanning material are the pyrogallol, 1,2,3-trihydroxybenzene tannins, which on heating give the parent substance pyrogallol; with iron salts, they give a blue-black. The pyrogallol tannins are accompanied by sugars which on fermenting give rise to organic acids; the catechol tannins have no sugar; it must be added. To the former group belong: myrobalan dried fruit; valonia, the acorn of the oak tree of Asia Minor; and the Sicilian sumach, with about 30 per cent for all of these. The tanners of Great Britain rely largely on these importations.

In addition to the natural tannins, synthetic tanning materials have been introduced, and applied successfully. Cresols, naphthalenes, and higher hydrocarbons are the raw materials for synthetic tannins, the "syntans." When cresol is sulfonated a sulfonic acid results; this when treated with formaldehyde condenses to form the tanning agent, Neradol D, polymerized or polycondensed dicresylmethane-disulfonic acid. It is a dark viscous mass, which is diluted, and partly neutralized before it is applied to the skins. The analogous condensation product from naphthalene-sulfonic acid is Neradol N, after dilution and partial neutralization, Neradol ND; it is polymerized or polycondensed dinaphthylmethane-disulfonic acid.[5] Ordoyal G is a similar product with a higher hydrocarbon as starting point.

These agents are true tanning agents, in that after application, they cannot be washed out, and in that the leather is heavier than the pelt. There are agents which penetrate the leather and become fixed, but on washing, the original pelt qualities and weight return; such agents are best named pseudotanning agents. Examples are fatty acids in organic solvents and aluminum salts.

Chrome Tanning. Chrome tanning is applied chiefly to the smaller kips and skins; on leaving the deliming bath they are bated, in order to reduce the plumbing which liming has caused and to render the grain smoother. This is done in a bath containing ammonium salts and small amounts of pancreatin (mainly tripsin). The effect of the ammonium salts is to reduce the p_H of the belt, and thereby their swelling. The addition of the ammonium salts is regulated so that the skins are brought to the optimal p_H range (7 to 9) of tryptic digestion and the removal of accessory hide proteins is thereby facilitated. Smoother grain and better "feel" of the final leather result. The progress of the bating is judged by the feel of the skins; skill is required to stop it at the proper time. Next the skins are pickled in a bath of dilute sulfuric acid which penetrates the structure and prepares for the chrome salt action; common salt is added to this bath to overcome the shriveling action of the acid. The skins are folded together and a number of them pressed free from water; as they leave the hydraulic press, they appear dry.

[5] "The industrial application of coal-tar products," H. M. Bunbury and A. Davidson, New York, D. Van Nostrand Co., 1925, p. 142.

In chrome tanning a salt of chromium takes the place of the vegetable tannins. A distinction is made between the one-bath type and the two-bath type. In the one-bath type the skins are placed in a wooden drum with a concentrated solution of basic chrome sulfate or chloride; the drum is rotated for 5 to 6 hours, which insures complete tanning. A quick test is to boil a small piece in water for five minutes; if the tanning is complete, the shape will not be altered. In the double-bath type the skins are drummed in a solution of sodium dichromate and hydrochloric acid for 3 hours; they turn yellow, and the chromium might be washed out. In order to fix it to the fiber, a solution of sodium thiosulfate (hypo) acidified with hydrochloric acid is placed in the drum and left for 4 hours; at the end of that time, the goods are blue throughout and permanently tanned. The product from either system is placed in a bath of borax and sodium bicarbonate; this is followed again by a water rinse.

A commonly employed chrome liquor is made by reducing a mixture of $Na_2Cr_2O_7.2H_2O$ and H_2SO_4 in equal proportions, with glucose. Another way, considered the simplest and safest to accomplish this reduction, is by passing sulfur dioxide into a solution of sodium bichromate.

The two-bath system had been patented some years before by A. Schultz and while modified in countless ways, is still essentially as first proposed. The amount of dichromate as $Na_2Cr_2O_7.2H_2O$ is 5 per cent of the weight of the skins; to this is added an amount of hydrochloric acid insufficient to liberate all the chromic acid; $2\frac{1}{2}$ per cent hydrochloric acid is used, while 4 per cent would be required, both in terms of 30 per cent HCl. For the second bath an amount of sodium thiosulfate, $Na_2S_2O_3.5H_2O$, twice or three times the weight of the dichromate is taken. An equal weight of potassium dichromate may be substituted for the sodium dichromate.

The goods are dried and may then be split if required. The splits are cuttings made by a knife resembling a band saw, kept sharp by constant contact with an emery wheel; the leather is fed in at a constant rate, grain side up; when only one split is made, the upper piece travels on the table of the machine,[6] the lower one drops to the floor. With thick leathers a number of splits may be made. Each split has the same area as the original piece, but is thinner. The split with the grain surface is made into shoe uppers; the other may be made into furniture leather, cheaper gloves, and traveling bag linings. If the leather is to be dyed, the dye is added to the fat-liquor, or in a subsequent bath. Logwood, in conjunction with direct blacks, is largely used for black, and acid dyes [7] for other colors. In order to produce a high gloss, so-called finishes, that is, pigments suspended in binders mainly consisting of acqueous solutions or emulsions of casein, albumen, shellac and waxes, are spread on the leather, and the piece is polished by friction in special machines and then placed between hot plates.

[6] Invented in 1809 by Samuel Parker of Newburyport, Mass.
[7] Chapter 26.

Sole leather is rarely made by the chrome process because it gives lower yields than the vegetable tannage. Further, chrome sole leather loses its shape and sometimes gets slippery. Vegetable tanning increases the weight of the leather, chrome tanning does also, but not to any greater extent; the former is sold by weight, the latter by area. An automatic machine measures the area in one passage of the skin; the total area is read off on a dial.

Chamois skin is made from the inner split of a sheep skin, by the oxidation of fish oils in the presence of skins. The American Indians tanned the buffalo skins by rubbing the brain into the dried skin. Velour leather is leather finished on the flesh side.

The by-products of the tanning industry are hair, which is used in plaster, and the small trimmings of the fresh hides, which are used for gelatin or glue.

GELATIN

The animal skin and the bone contain collagen; as noted under leather, the corium of the skin is 75 per cent collagen on a dry basis. Bones are one-third collagen by weight. Gelatin is valued for its power to hold many times its weight of water in the form of a semi-solid, called a gel, and for its power to retard or prevent the formation of crystals. A 3 per cent solution in water forms a jelly when cold.[8]

The skins used for making gelatin are rarely the perfect skins fit to make leather, but the trimmings in the hide house, and occasionally imperfect skins. The bones come mainly from near-by slaughterhouses and butcher shops, but also from long distances, such as heads from South American cattle; these often come with the horns attached. The horn pith gives gelatin, but not the horn proper. Hoofs yield no gelatin whatever. Sinews and tendons are suitable. Strict government regulations govern the selection of raw materials for the manufacture of edible gelatin, and require laboratory control of all the phases of manufacture. Glue is made from the same raw materials, but no government regulations apply.

Gelatin must be prepared with water at a temperature as low as possible in order to prevent excessive hydrolysis, which is accompanied by a loss in jellying power. To that end, bones and skins are pretreated with lime which renders the preparation easier; it is done at 70° C. and in a short period. Glue may be considered as gelatin which has been hydrolyzed further; its jellying power is low, also its water-absorbing power (imbibition), but its adhesive power is greater than that of gelatin.

Bones are first freed from grease by heating them with steam under pressure, releasing the pressure to a few pounds just before opening the kettle; the grease floats on the water and may be run off. It is utilized in soap making. A better way is the extraction by means of a low-boiling petroleum naphtha, because there is no loss of gelatin-forming substance by this method. In many plants the bones are transferred

[8] Gelatin with pH = 4.6 acidity has maximum jellying power; above or below, it is less.

over a belt conveyor which passes over a magnetic separator, placed at the turn of the belt. The bones drop off into a chute leading to squirrel-cage disintegrators where they are crushed, while any iron present is carried a short distance on the under side of the belt and then drops off into a receptacle. The crushed bones are hoisted to the top of a central tower by a bucket elevator and delivered through chutes to any one of a number of wooden tanks. These tanks may be of various sizes; large ones are 20 feet in diameter and 5 feet deep; four tanks form a battery and are operated in series on the countercurrent principle. Cold dilute hydrochloric acid (5° Bé., 7.15 per cent HCl) meets the most nearly exhausted bones; while nearly spent acid overflows into the tank containing the fresh bones. The mineral matter of the bone, mainly calcium phosphate and carbonate, dissolves, leaving the organic matter, the collagen, with the original shape of the bone. Collagen so prepared from bones is called ossein. It may be treated further at once, or shipped to a distant factory. The latter procedure is sometimes economical if the ossein plant is located near a heavy chemical plant, so that the hydrochloric acid can be pumped through glass lines directly into the ossein plant, avoiding the rail transport of the acid.

Skins do not need the preliminary acid treatment since their collagen is not masked by mineral salts.

The ossein is placed in 5-foot cubical concrete vats, of which there are several hundred, with slaked lime and water, and left there for a month or longer. The ossein swells and turns snow white; the mucins and albumins are dissolved, and any remaining grease is saponified. At the proper time,[9] the ossein is removed to a rotary tank and washed with four changes; first with water, then with dilute hydrochloric acid, then twice with water; the cycle in the washer is one day. The ossein is then ready for extraction. Skins are treated in the same way; they become translucent.

The extraction of the limed ossein or skins is performed in wooden tanks 4 feet broad and 4 feet deep, with a steam coil under a false bottom; the charge rests on the false bottom and thus does not come in direct contact with the coil. The water is maintained 60° C.; in 8 hours a first extract containing 8 to 10 per cent gelatin is formed; it is filtered and cooled. A second extraction is made at the same temperature, or a few degrees higher; a good strength is obtained; the liquor is filtered and cooled. A third extract is made at about 75° C., but this will be too weak to jelly on cooling, so that it is concentrated in a vacuum to the jellying strength. The third run is darker and has a lower jellying strength; it is still edible, but is used for its water-retaining power chiefly, in marsh-mallow confectionery, for example.

The reaction which takes place during extraction is probably as follows:

$$C_{102}H_{149}N_{31}O_{38} + H_2O = C_{102}H_{151}N_{31}O_{39}$$
collagen   *gelatin*

[9] If the liming is continued too long, ammonia is evolved, and the material is spoiled.

The filtration of the warm gelatin solution is done in a special circular filter, shown in Figure 186; the filtering medium is wood pulp; the solution passes from the entering space near the shell to the central channel. In order to reach the central channel a considerable layer of wood pulp must be passed; here the solution deposits the suspended particles which cause cloudiness. The gelatin solution from the filter is placed in long steel troughs 6 inches deep and 6 inches wide, and cooled in refrigerated rooms. The resulting solid jelly is removed from the mold and
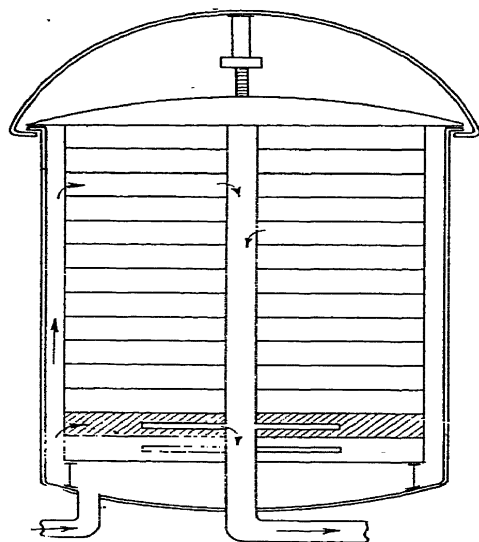
FIGURE 186.—Filter press for gelatin solution.

cut by hand into strips one-half inch by 2 inches and 6 feet long. These are laid on galvanized iron or monel metal wire set in frames, stacked on small trucks and shoved into tunnels 70 feet long through which filtered air heated to 40° C. is pulled by an exhauster. The gelatin strip dries to a thin sheet which still contains about 10 per cent of moisture; this amount is not removed. The strips are usually ground to a coarse powder for greater ease in handling.

Uses of Gelatin. Gelatin is a food, easily assimilated; it is valuable also mixed with other foods because it disseminates the particles; with fats and oils it forms an emulsion which greatly facilitates the digestion, hence its use with meats and in desserts. Its use in ice cream is due mainly to its function as a protective colloid; it prevents the formation of crystals of sugar and water during the storage period, at the temperature of − 10° F.; the proportion of gelatin sufficient for this result is 0.5 per cent. About 2400 tons of gelatin are used per year in the United States for this purpose. Its use in confectionery has been mentioned. All these uses together account for a yearly consumption of over 10,000 tons of edible gelatin in the United States.

Gelatin is used for capsules in the pharmaceutical houses; the hard two-piece telescopic capsules are gelatin alone; the flexible capsules contain also glycerin. In the manufacture of photographic plates, films, and moving picture films, gelatin is used for the sensitized coating which holds the silver salts. It has many other minor uses.

When gelatin is made from bones, there may be obtained as a by-product dicalcium phosphate, or by using more lime, tricalcium phosphate; the former is used as a fertilizer, the latter in the potteries for "bone china." Calcium chloride is formed at the same time, and is usually wasted. Grease as a by-product has been mentioned.

GLUE, AND "PELLET GLUE" PROCESS

The manufacture of glue is identical with that of gelatin, except that the raw materials need not be selected with such care. The extraction of the glue stock (ossein, limed skins) may be performed in a single "boil," but four extractions of shorter duration are preferable; the liquor is concentrated to perhaps 15 per cent in vacuum condensers. This con-
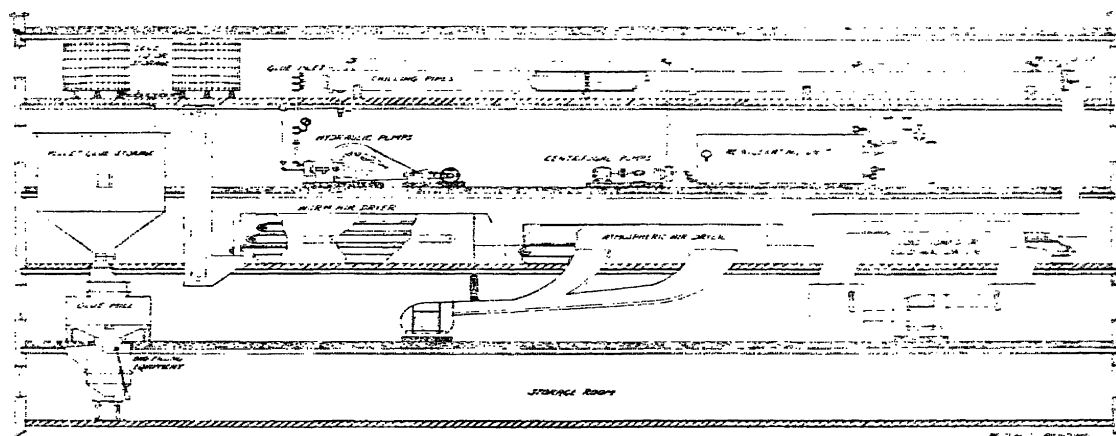
FIGURE 187.—Lay-out of a pellet glue plant. (Courtesy of Darling and Co., Chicago.)

centrated liquor is congealed in thin layers, and these are dried in a tunnel drier. A preservative is added to the concentrated solution (borax, formaldehyde); this cannot be done for edible gelatin.

Instead of drying the chilled strips of glue in tunnel driers, a new method has been devised by Thomas K. Lowry, in which pellets of glue are formed and dried in a continuous process, eliminating the tunnel drier and all the hand-labor it involves.[10] The 50 per cent glue solution is chilled, and forced through wire grills; a revolving knife cuts off (scrapes off) the protruding lengths into small pellets of equal size. The pellets pass through a three-stage system of drying. The first stage operates

[10] *Factory and Ind. Management*, **82**, July (1931), published by McGraw-Hill Book Co.

at 70° F. In this drier stage, the pellets are kept in constant motion by automatic rakes. In the second stage the temperature is 100° F. and in the third, up to 130° F. Pellet sizes vary from $\frac{3}{16}$ to $\frac{3}{8}$ inch. The time in the first drier is 3 hours, in the second 6, and in the third 9. The total time is therefore 18 hours, instead of the 2 to 6 day period required by the older method. Figures 187-188 will help make the procedure clear.

Another method is the dropping of the glue pellets into hot toluene.
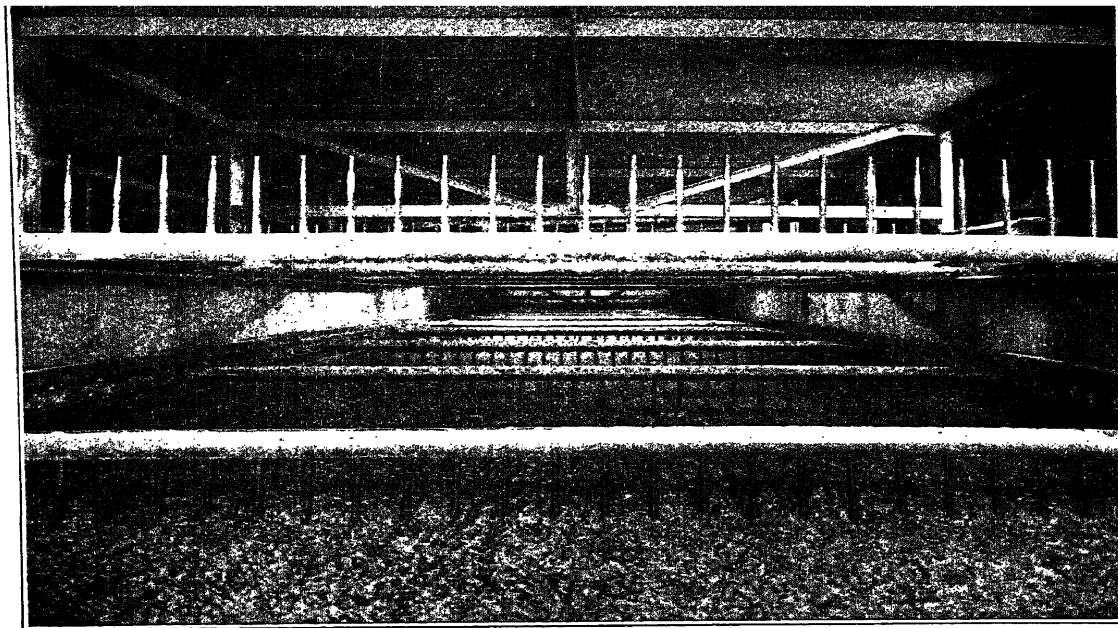
FIGURE 188.—The Thomas K. Lowry process for producing glue in the form of dry pellets. First stage drier, operated at 70° F., with rakes on an endless chain. (Courtesy of Darling and Company, Chicago.)

The removal of grease from glue is essential, because it interferes with the adhesive power. A practical test is to make a 5 per cent solution, add a water-soluble dye, and paint this on a white board. Examination with a hand lens will reveal white spots if grease is present.

A strength test is made by gluing together two wooden blocks and after a definite time, placing them in a machine which measures the force required to pull them apart.[11]

Animal glue of the best quality is still unsurpassed for strength; it is used in furniture making, in veneering, book-binding, rug-sizing, in making the tips for matches, in sizing straw hats, for making sand paper.

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[11] Glue has maximum strength when its pH is 7.0; glue contains considerable calcium combined as calcium gelatinate.

emery, carborundum, and other abrasive papers. With waste leather, it makes imitation leather; ground cork is made into shapes with glue. A waterproof animal glue is made by adding tannins or formaldehyde.

Other Adhesives. Fish glue is made from the skins of the cod, cusk, and other fish; the washed material is heated with water and concentrated; phenol may be added and a little oil of wintergreen (synthetic) in order to mask the odor. Isinglass is the dry glue made by boiling the air-bladder of the sturgeon.

Fresh casein boiled with water has adhesive properties; once set, moisture does not weaken it. Starch paste or British gum is made by digesting starch with dilute acids. A solution of sodium silicate is an adhesive; it is not strong, but sets quickly, and is valuable in the manufacture of cardboard boxes and corrugated paper. Mucilage is a solution of gum arabic or acacia in water. Marine glue is merely a name for a waterproof adhesive containing rubber, shellac, and naphtha.

TABLE 71.—*Production of Gelatin and Glue in the United States in 1925 (Bureau of the Census).*

	Pounds	Value, cents per pound
Glue:		
animal	92,325,806	10
vegetable	126,792,581	4
Casein glue	13,415,275	11.5
Flexible and fish glue	11,763,502	16.5
Gelatin:		
edible	20,780,571	34
inedible	2,953,869	4.4

Theory of Tanning. The study of tanning, and of the nature of glue has led to the important branch of chemistry called Colloidal Chemistry which includes in its considerations the combinations due to forces between surfaces, and at those surfaces, such as droplets, grainlets, or bubbles of microscopic dimensions, in a gas, liquid or solid; while pure chemistry concerns itself primarily with forces and events within the atoms and molecules, and between them. For the combination of tanning agents with the collagen of corium a simple reaction cannot be written. In the tanning process, the tanning agent is more or less irreversibly fixed by the hide protein whereby its hydrophillic centra are changed into hydrophobic (dehydrating, water-repelling) groups. Resistance of the product toward the action of proteolytic agents is thus acquired.

It was the substance glue, the first one studied with respect to surface forces, which gave its name to the branch of the science.[12]

OTHER PATENTS

1,848,506, thiophenol tanning and mordanting agents; 1,851,021, producing water-soluble tanning agents which comprises condensing a methylol compound of a monohydric phenol with resorcinol at a temperature below 50° C., in the presence of water and a condensing agent; 1,844,018, a new tanning composition comprising the halogenated reaction product of sulfite cellulose and hydrogen peroxide;

[12] The Greek word for glue is kolla.

1,895,446, process for producing a transparent clear bone glue or bone gelatin solution; 1,895,433, on improving water-resistance of casein glues, by treating with a polymerized acetaldehyde; 1,858,193, manufacture of vegetable-tanned sole leather; 1,881,763, process for cold dressing and drying leather; 1,753,694, leather finishing compound consisting of crude oil, sweet oil, cod liver oil and glycerin; 1,744,756, a leather-stretching and tacking machine; 1,892,599, a process for the manufacture, sterilization and puffing of gelatin; 1,310,148, apparatus for stretching and drying leather.

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Photography plays an important part in modern life; it serves not only for artistic photography, such as portraits and landscapes, but for numerous scientific and medical purposes. The photographic film is superior to the human eye in that it is sensitive to wave-lengths of light to which the former is insensitive. It is to photography that we owe the inexpensive entertainment of the moving picture.

Chapter 37

Photographic Plates, Films, and Papers. Lithography

Photography has passed through several stages on its way to its present position of almost universal service. Originally developed as a means of quickly recording stage settings (Daguerre), it became a replacement for painting, a hobby. With the introduction of gelatin and later of the flexible celluloid film, the present dry plate and rolls of film became possible, and were improved more and more, allowing exposures of very short duration, and finally reaching their present state of perfection. Pictures of landscapes, perfect and sharp, are taken as a matter of routine from aëroplanes traveling 100 miles per hour, with exposures of one three-hundredth second.[1] Astronomy relies for its evidence on photographic records of the position of the stars and of their motion.[2] The microstructure of metals and alloys is studied by photography. The absorption of light in the ultra-violet (shorter wave-lengths than blue) and infra-red (longer wave-lengths than red regions), to both of which the eye is insensitive, is revealed by photography. The selective absorption of X-rays by teeth, bones, metals, and coated animal organs, gives opportunity for photographic records indispensable in modern diagnosis and surgery. Portraiture has become a fine art. In periods of war emergency, the camera with a telephotic attachment, operated in an aëroplane, observes in an instant more than the human eye could in an hour, and yields its information, independent of memory, in a way which allows its leisurely study. A valuable contribution was also made in developing the film roll and film pack, which may be introduced and removed from the camera in full daylight; it has greatly stimulated amateur photography. The crowning social achievement of photography is the life-like motion picture and the "talking" pictures in which sounds are recorded and reproduced photographically.

All the uses of photography listed above depend upon the action of light on silver bromide, with a certain amount of iodide admixed. In blue prints, much less expensive iron salts are used, and the development

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[1] Erie County, N. Y., has been photographed from the air, so that a complete map showing roads, rivers, bridges, and buildings is available; the elevation of the aëroplane was 9500 feet.

[2] The Einstein theory that light is deflected by astral bodies is tested photographically; also the details of an eclipse.

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is simple and cheap, so that blue prints have become the means of recording drawings and tabulations of all kinds.

The present dry plate and dry film were preceded by a plate which was sensitized just before using, and without drying (wet plate); this method is still useful in certain branches of commercial work. Still another method of photographing depends upon the hardening action of light on albumen containing sodium dichromate, and this principle is applied on the large scale in lithography by the zinc plate method.

FIGURE 189.—X-ray picture of a tulip. Note the vein structure in petals and leaf. (Photographed by M. C. Reinhard, M.A.. Buffalo, N. Y.)

The Light-sensitive Emulsion. For dry plates, films, and (silver) papers, the light-sensitive part is the coating of gelatin in which silver bromide crystals with some silver iodide crystals are disseminated; the gelatin coating is the essential part, the glass plate, the flexible film, or the paper furnishing merely a suitable support.

The gelatin used is made from calf skins.[3] A solution of potassium bromide with some potassium iodide is prepared, to which 3 per cent gelatin is added, and to this solution, lukewarm, a water solution of silver nitrate is added; the silver bromide which forms remains in suspension by virtue of the protecting action of the gelatin. After the silver nitrate solution has been added, and in some plants after "ripening"

[3] Chapter 36.

(as explained further), the gelatin content is raised to 7 per cent. This strong gelatin suspension, really a colloidal solution, is commonly called the "emulsions"; it is cooled to a soft jelly,[4] and made into "noodles" which are placed in water for the purpose of removing the potassium nitrate formed as the second product in the reaction $AgNO_3 + KBr = AgBr + KNO_3$. If the ripening process has not been performed with the 3 per cent gelatin, it is performed with the 7 per cent gelatin, before the washing. Pure water is not used for washing, but a solution of calcium sulfate, because the latter does not swell the gelatin as pure

FIGURE 190. — Pyelogram, an X-ray picture showing the ureter and the kidney cavity, by injection of 15% sodium iodide through the bladder. (Courtesy of M. C. Reinhard, M.A., Buffalo, N. Y.)

water would. The excess potassium bromide is dissolved as well as the potassium nitrate formed.

Ripening. In order to raise the sensitivity (speed) of the emulsion, it is maintained at 32° C. for 6 to 7 days, or at a higher temperature; the heating causes the gelatin to lose its jellying power, and for that reason, the 3 per cent solution is heated, and fresh gelatin added at the end. The proportions of bromide and iodide (34 of the former to 2 of the latter) to silver nitrate is greater than required for the reaction, so that there remains an excess of potassium bromide; this must not be removed before the period of heating, for without it, no ripening, no increase in the sensitivity takes place. The period is regulated ac-

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[4] There is no difficulty in obtaining a jelly; for even a 3 per cent gelatin solution forms a solid gel at room

cording to the degree of sensitivity desired, which is the higher, the longer the heating; but there are other factors which help regulate speed. The greater the proportion of silver salts to gelatin, the faster [5] the plate; furthermore, silver bromide alone is more sensitive than the bromide with iodide addition. It is not uncommon to blend various batches of emulsion. If the ripening is at a moderate temperature, the jellying power of the gelatin is not impaired, and the ripening may be performed with the 7 per cent gelatin. There are many modifications of the procedure just described.

The warm emulsion is then placed in cheese-cloth bags, and pressed under cold water; the stringlets of emulsion coagulate and form a product resembling noodles. These may then be washed in the cold calcium sulfate solution mentioned before, without dissolving; only the water-soluble salts which are not wanted pass out in the water.

The washed gelatin in noodle form is remelted, and there is added at this point some alcohol, a very little thymol as a preservative, some chrome alum, and some potassium bromide as a retarder; all these substances are in solution. The alcohol helps the flow of the emulsion, while the chrome alum hardens it. The emulsion is now ready to flow onto the glass plates or film, and is allowed to set by cooling. For the films especially, a preliminary undercoat is advisable, which will bind the emulsion sheet to the pyroxylin; it consists of gelatin solution with chrome alum and acetone.

Plates and film [6] are then dried in a current of warm, dry, filtered air. Photographic paper is coated in the same way as plates and films, but as a rule, the emulsion for plates and films is much more sensitive than for paper. A specially made paper is coated with a white pigment, usually blanc fixe, then examined for defects, and finally coated with the light-sensitive silver salt emulsion, generally in albumen. For enlargements, a paper more sensitive than the usual contact paper is made.

Making the emulsion, ripening it, coating plates and films as well as paper, and drying, must be performed in a dim red or orange light.

Camera. The plate is exposed in the camera (plate holder) which for short exposures must have a lens allowing maximum light to enter, and a good shutter. Improvements in lenses and shutters have kept pace with the advances in plate and film manufacture. For moving pictures a special camera is now obtainable for amateur use (with 16 mm. film, instead of the standard 32 mm. width).

Developing and Fixing. The exposed plate (or film) is placed in an alkaline developer in the dark room; the developer causes metallic silver to form at the spots affected by the light, and the depth of the silver deposit is proportional to the intensity of the light. After the

[5] A fast plate requires a short exposure only; a slow plate, a long exposure; in the usual emulsion the silver salts are 30 per cent of the total.

[6] Chapter 35 has a description of the camphor-containing film; see also *Tariff Information Survey*, N25 (1921).

picture has appeared and has begun to disappear, the plate is removed from the developer, washed in water, and placed next into a solution of sodium thiosulfate (Chapter 4), which removes the unchanged silver salt, thus fixing the image. After washing, the plate is dried, and is the negative. From the negative, a positive is printed on paper.

The alkaline developers are hydroquinone HO⎯⎯OH, pyrogallol 1,2,3-trihydroxybenzene, metol or methyl-para-aminophenol OH⎯⎯NH.CH$_3$, in the form of sulfate: and eikonogen or sodium salt of α-amino-β-naphthosulfonic acid. These are called alkaline developers because they are used in a solution of sodium carbonate. Sodium sulfite is also added in order to prevent oxidation by the air, and a little potassium bromide to retard the development of the unaffected silver bromide. Amidol is used without alkali; it is diaminophenol-hydrochloride 1,3,4-C$_6$H$_3$.(OH)(NH$_2$)(NH$_2$HCl). One developer may give a green-black, another a brown shade of black; as a rule, a mixture of two developers is used to give deep blacks.

For moving pictures, it is convenient to make a negative, from which any number of positive films may be produced.

The explanation of the action of light on the rapid photographic plate or film is as follows: In the silver bromide lattice (which makes up the grain or crystal embedded in the gelatin) there are sensitive centers due to the presence of silver sulfide molecules. Wherever there is present a silver sulfide molecule, the normal lattice is distorted, for Ag$_2$S does not fit into the Ag$^+$ and Br$^-$ system. At each place of distortion, an exceedingly slight energy impulse will suffice for the liberation of a free silver atom, whereas an amount of energy thousands of times greater would be required to liberate a free silver atom from the normal undistorted silver bromide lattice. Translated into photographic terms, the distorted lattice results in a fast plate, the undistorted lattice makes a slow plate or paper (such as the old Solio print-out paper).

The silver sulfide has its origin in an impurity of the gelatin, present in exceedingly minute amounts, allyl mustard oil; this substance reacts with silver bromide to form, after several intermediate compounds, silver sulfide finally.

The invisible latent image consists of a minute amount of metallic silver, and this slight amount becomes the nucleus for further deposition of such silver as the developer produces from the silver bromide.

The photographic dry plate prepared from the gelatin emulsion of silver bromide is sensitive to wave-lengths in the green, blue and violet, the region of 500 mμ to 400 mμ. By adding a dye such as erythrosine, ethyl red, pinacyanol, orthochrom, to the emulsion, the resulting plate or film becomes sensitive to yellow, as well as to green, blue and violet; such plates are called orthochromatic. By the use of polymethine dyes,

plates sensitive over the whole of the visible spectrum are produced, the panchromatic plates.

In order to photograph in the infra-red, in the region between 700 and 800 mμ, kryptocyanine is the dye added to the emulsion, while for the region beyond 800 mμ, as far as 1014 mμ, a plate sensitized with neocyanine will record the light. In this fashion, the photographic plate can reveal light waves invisible to the eye, and longer in wave-length than red light.

In the ultra-violet, good records are obtained with panchromatic, or ordinary plates in the region between the violet and 320 mμ. Below 320 mμ, to about 200 mμ, the plate may be made sensitive by covering it with a thin layer of petrolatum, so that the invisible light of wave-lengths shorter than violet may also be caught by the photographic plate.

An additional striking advance has been made. After a highly sensitive plate has been exposed, it may be bathed in a solution of pheno-safranin, with the result that its sensitivity to light is reduced so considerably that it may be developed by ordinary lamplight, with perfect results. This is called desensitizing.

Wet Plate Process. The wet plate process is older than the dry plate, but is still used for commercial work, such as in lithographic plants. The same glass can be used over and over, after the negative is no longer needed. It is coated with collodion (pyroxylin dissolved in ether-alcohol) containing potassium bromide and some iodide, dried for a few moments, and bathed in a solution of silver nitrate; the excess solution is allowed to drain off, and the plate is ready for exposure. It is developed by means of a solution of ferrous sulfate in dilute sulfuric acid; the negative image appears in metallic silver as with the dry plate. The unchanged silver bromide is removed by a dilute potassium cyanide solution. The negative may be intensified by means of copper sulfate and potassium iodide solution, followed by silver nitrate. Finally a solution of sodium sulfide converts the image to a jet black.

In dry-plate photography, a faint negative may be intensified by means of a solution of bichloride of mercury followed by ammonia; a picture which is too dense on the other hand may be reduced by means of ammonium persulfate; there are several other formulas.

COLOR PHOTOGRAPHY

Transparencies in the natural colors may be obtained by photography; of the several plates available, that of the Lumière brothers is the easiest to handle. It consists of a glass plate coated with a layer of starch granules of three colors, violet, red, and orange; over the starch layer, the sensitized gelatin layer is placed. The plate is exposed glass side out, so that the light must pass through the granules before reaching the gelatin. A single red flower for example would send its rays through red granules, behind which the silver bromide would be affected.

On developing, only these particles of silver bromide would change to metallic silver. The procedure at this point is different from that for ordinary negatives, for the picture is reversed, as follows: After washing in water, the deposited silver is removed by a solution of potassium permanganate in sulfuric acid. On looking through the plate, the red granules forming the flower are now clear; there remains only to block all the other granules. This is done by taking the picture into daylight, immersed in the original developer. The unchanged silver bromide is changed to metal, permitting no light to pass, so that only the image of the red flower appears on holding the plate against the light.

Color films are in process of development. Color plates and films are used in medical studies.

LITHOGRAPHY

The word lithography has come to mean the printing from stone or metal in several colors, partly superimposed to reproduce an original artist's painting. The metals are used in rotary presses. Either aluminum or zinc sheets are employed; they are used over and over again, but the surface must be suitably grained before application of the printing image. Stones are not favored any more, except for small work and special studies. The preparation of the metal plate images is largely a photographic process. It is appropriate to discuss lithography in this chapter for another reason: the first utilization of the action of light on chemicals was in lithography (Niepce), preceding photography proper.

In stone lithography, fine-grained limestones (from Bavaria) are covered by hand drawing, with the lines and areas of a single color. The stone is treated with dilute nitric acid for a brief period, which attacks the uncovered portions, leaving the greased portion slightly raised. The stone is placed in a back-and-forth press, and touched at one end by a water-wet roller, further on by an inked roller (paint); the bare stone is moistened, while only the greased portions take the ink.

For the zinc-plate process, the single colors are selected not by the human eye, but by the camera. The original artist's painting is photographed three times (or more), each time through a screen which blocks off one color, but allows the others to reach the gelatin plate; to make this point and the subsequent ones clearer, a yellow vase may be selected. The first picture is taken through a violet screen which stops yellow but allows blues and reds to pass; hence the vase will be represented in the developed and fixed plate by clear glass (1). A positive is now made, through a screen of fine black lines (diamond-shaped openings, with 133 lines to the inch); the positive obtained is in the form of dots, which allow gradations in intensity (2). This positive is on ground glass, and is retouched; the yellow flower is represented by a deposit of silver, while the rest of the plate is clear glass. A second negative is made (3), again retouched, and used finally for the preparation of the zinc plate (4). In

the second negative, the yellow flower is again represented by clear glass, so that the positive made from it, on the zinc plate, receives a flood of light wherever there is yellow in the original painting.

The zinc plate is coated with a solution of albumen containing ammonium dichomate; the solution is spread evenly by tipping the plate; after drying with a small electric fan, the plate, hung vertically, is ready for exposure. It is exposed under negative (3) in the special movable arc lamp. The size of the zinc plate varies, but is perhaps 4 feet by 3 feet; the negatives are of various sizes, but frequently of the size of a magazine cover. The zinc plate is large enough to accommodate a number of images, sometimes as many as 25 or 30. The albumen-dichromate layer becomes insoluble by the action of the powerful arc light. The exposed metal plate is laid on the table in the dark room, and covered completely with a liquid wax containing a black pigment. Cold water is flushed over it while a turntable spins it around; light pressure from a sponge helps remove the unaffected portions of the albumen, while the affected portions remain and are now visible. The developing over, there remains only a treatment with chromic acid and phosphoric acid, and gum acacia.

The zinc plate is mounted on the cylinder of a rotary press, and moistened with water by one roller, while another roller presents the ink or paint; the bare zinc takes the water, but the waxy surface of the image repels it; the ink on the other hand is repelled by the wet metal, but is received by the waxed image. On pressing against the paper, the yellow flower is reproduced in yellow ink with the exact gradations in intensity. In a second press, a zinc plate for the red will have been prepared, and will print, on the sheets already bearing the yellow portions of the picture, whatever was red in the original painting; in a third, the blue will be applied. A fourth with gray and a fifth with the black are common, and the number runs as high as eight, with a corresponding increase in beauty and also in cost.

Printing from zinc plates bearing several images is called multiple printing; the roll makes 3000 to 3600 r.p.h. and for each revolution, a sheet with perhaps 25 images is inked.

In the "deep-etch" process of more recent introduction, the zinc plate is coated with a special gum-containing coating, and exposed under a positive. The unexposed parts are cleared by means of a hydrochloric acid solution containing zinc chloride. The bare metal is etched, and impregnated with ink; this is the image which will print in the press. The protected parts of the coating are now removed, and the metal surfaces desensitized by gum acacia and nutgall solutions. In the "deep-etch" plate, the ink, hence the image, is seated on the metal, just as in the old "transfer" plates; there is no film of albumen to wear away. It has been deservedly successful.

The value of photographic materials such as plates, moving picture (unexposed) and other films, paper, chemicals for developing and fixing,

exceeds 40 million dollars per year, for the domestic production (U. S.) alone. From France, moving picture films (unexposed) imported yearly are worth one-half to one million dollars. Cameras, including motion picture cameras, were \$4,604,479; films, motion picture and others, \$40,8999,597; sensitized paper, \$13,622,206; plates and slides, \$944,717; total photographic apparatus, materials, and projectors, \$69,874,994, all in the year 1935 (U. S.).

Blue Prints. The light-sensitive paper used for blue prints consists of white paper coated with a solution of ferric ammonium citrate and potassium ferricyanide; the coating is done automatically, in rooms with subdued light. An India ink tracing on cloth supported by a coat of pyroxylin is placed between the sensitized paper and the source of light; the black lines protect the coating, but elsewhere the iron of the citrate is reduced (from ferric to ferrous). On immersion in water, the unaffected mixture dissolves while the reduced iron forms the insoluble blue ferro-ferricyanide [7]; the fixing agent is merely water. The result is a design of white lines on a blue field. A strong light must be used, such as direct sunlight for 15 minutes; arc-lights are the modern practice in plants requiring many blue prints.

Of increasing importance is the process known as photostating, in which the page of a book, print, or picture is reproduced as a paper negative by the reflection of strong light; the negative may then in turn the illuminated, and made to produce a positive. The paper used is a silver bromide paper. No plate nor film is necessary.

<div align="center">OTHER PATENTS</div>

U. S. Patent 2,005,837, manufacture of photographic emulsions; 1,991,136, photographic emulsion; 1,787,564, manufacture of fire-proof photographic films; 1,890,026 and 1,890,490, apparatus for propelling long strips of films, such as motion picture films, through a liquid bath; 1,815,513, manufacture of films from an aqueous cellulose solution; 1,889,818, apparatus for developing photographic films; 1,860,059, apparatus for developing roll films; 1,742,814, machine for assembling photographic films; 1,836,023, lithographic printing machines; 1,820,593, lithographic plate and process of preparation.

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[7] Ferri-ferricyanide is not blue, but brown-yellow, and soluble in water.

Chemical fertilizers play an important rôle in increasing the crops of grains and cotton. In another way, chemical science has made itself almost indispensable to the agriculturist, in the killing of insects which render the fruit wormy or destroy the foliage, and in the control of fungi which spot the fruit and destroy the trees or vines. Such crops as the potato, tobacco, and cotton are all subject to pests which are successfully fought by means of chemical poisons.

Chapter 38

Insecticides, Fungicides, Disinfectants

The application of chemical substances below the soil provides the plant with extra food which permits better growth resulting in a greater yield per acre; but above the soil, the plant also stands in need of the products of chemical science, in the form of insect killers (insecticides) and fungus destroyers (fungicides). The apple tree alone for example is subject to the following insect pests: the codling moth, the San José scale, the aphis, red bug, apple and thorn skeletonizer, bud moth, apple maggot, gipsy moth, canker worm, and nine more.[1] In addition it is subject to fungous diseases such as the apple scab, cedar rust, and several others. The proper choice of chemicals is determined by experiments performed at State and Federal experimental stations, and the knowledge so obtained is offered free to the agriculturist. The method of application is by spraying a suspension of the chosen materials in water, or by "dusting" the powdered dry material; in general spraying is better, and more widely practiced. The system of protecting crops in this way has become of great importance and wide application, so much so that unsprayed fruit is essentially unsalable. The most important substances employed are lead and calcium arsenates, sulfur, lime-sulfur, Bordeaux mixture, kerosene and other emulsions, and powdered poisonous plants. For certain diseases such as the fire blight, a bacterial disease (apple tree), the remedy is to cut off the affected branches and twigs in the wintertime, and to disinfect the cuts with a solution of mercury bichloride ($HgCl_2$). The destructive insect pests are held in check also by birds, toads, beetles, and parasitic insects; other means of protection are the banding of the tree trunks with sticky materials to prevent the ascent of caterpillars and wingless moths, band traps, and local application of the fire torch.

INSECTICIDES

The agricultural insecticides may be divided into three classes: *a.* The stomach poisons, for the insects which eat the foliage; these include arsenate of lead, arsenate of calcium, hellebore, and Paris green. *b.* The

[1] "Injurious insect pests and fungous diseases," *N. Y. State Dept. Farms and Markets Cir. No. 292*, 3-10 (1925).

contact insecticides, effective against the insects which do not eat the foliage, the boring insects; to this group belong lime-sulfur, nicotine dust, and kerosene emulsions. *c.* The fumigants, used against borers which are not reached by sprays, and for the protection of grain stored in warehouses; some of the substances in this class are carbon disulfide, hydrocyanic acid, ethyl acetate-carbon tetrachloride mixture. The divisions are not strict, for one substance may serve in two classes.

The Stomach Poisons. The yearly production of lead arsenate in the United States is 15,000 tons, and of calcium arsenate, somewhat higher; Paris green is lower in tonnage, about 2500 tons. The production of these three substances depends upon arsenic, usually arsenic trioxide or white arsenic, and a discussion of their manufacture will of necessity include a few words about the availability of arsenic trioxide.

White arsenic, As_2O_3, is a by-product of the smelting of copper and lead; it passes out with the fire gases and may be collected in settling chambers, in bag filters, or in the Cottrell electrical [2] precipitator. The removal of the arsenic dust is obligatory in many States, so that a certain source for white arsenic is assured; it is, however, also obtained by roasting arsenic sulfide ore and other ores, in which operations it is the primary product. If the copper smelters work to capacity, the Anaconda smelter (Montana) alone could supply 10,000 tons annually from its Cottrell precipitator.[3] Capacity has not been reached in recent years. In 1935, there were produced 14,237 tons of white arsenic, in two grades, the crude priced at $34.30 a ton, the refined, at $51.20 a ton; there were imported besides, 15,075 tons, of which 60 per cent came from Mexico. The consumption is due in large part (86 per cent) to the manufacture of arsenical insecticides, to a lesser extent to the manufacture of plate glass. Because of the rapid growth in the use of lead and calcium arsenates, the yearly consumption of white arsenic will undoubtedly increase.

White arsenic heated with Chile saltpetre gives sodium arsenate, Na_2HAsO_4, and this in solution may be used to make the lead and calcium arsenates. Other ways to change the white arsenic, As_2O_3, to arsenic acid, H_3AsO_4, are: by means of chlorine in presence of water [4] followed by sufficient concentration to drive off the hydrochloric acid formed in the reaction and by heating with nitric acid and evaporating to a syrup. Lead arsenic is made by suspending litharge, PbO, in a solution of arsenic acid in the presence of nitric acid or acetic acid [5]; an improvement is to use sublimed lead oxide (yellow) (PbO) made into a cream with water, and add to this the solution of arsenic acid.[6] The reaction takes place at room temperature; the lead arsenate precipitates

[2] Chapter 43.
[3] *U. S. Tariff Information Survey*, FL6, U. S. Tariff Commission, Washington, D. C., 1921, p. 11.
[4] U. S. Patent 1,169,114.
[5] U. S. Patent 892,603.
[6] U. S. Patent 1,228,516.

and is filter-pressed and sold as a paste, or, as is becoming the general custom, is dried and shipped as a powder.

The precipitate does not settle very well; indeed it is essential that it should remain in suspension for long periods when made up for spraying; a proposal was made to avoid any kind of washing by adding magnesium hydroxide, $Mg(OH)_2$, after the lead oxide had reacted, to bind the remaining arsenic acid or arsenate of sodium.[7] The resulting product is a mixture of magnesium and lead arsenates, $MgHAsO_4$ and $PbHAsO_4$, which is said to be an excellent insecticide.

An excess of lead is always provided, for soluble arsenic beyond a certain figure (1 per cent As_2O_3) is prohibited by the Federal Insecticide Act of 1910. When lead nitrate is treated with arsenic acid, the acid lead arsenate, $PbHAsO_4$ precipitates and remains in suspension even better than the neutral salt, contains more arsenic, and is quicker in action on the insect. When lead acetate is used instead of the nitrate, the neutral lead arsenate, $Pb_3(AsO_4)_2$, is formed which is less injurious to foliage, and remains in suspension very well; it is used for peach and plum trees. In the process using lead oxide, the kind of lead arsenate formed is determined by the amount of lead oxide used to a given amount of arsenic acid. Both the acid lead arsenate and the neutral lead arsenate are insoluble in water.

$$PbO + H_3AsO_4 = PbHAsO_4 + H_2O; \quad 3PbO + 2H_3AsO_4 = Pb_3(AsO_4)_2 + 3H_2O.$$
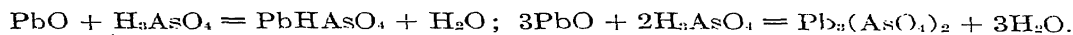
Lead arsenate may also be manufactured in the dry way, by burning powdered lead sulfide or metallic lead and white arsenic in a blast of hydrocarbon fuel; the oxidation and combination occur in the high heat of the burning fuel. The lead arsenate formed is collected in settling chambers and bag filters.[8]

Calcium arsenate, also a white powder or paste, is made by running a solution of calcium chloride, $CaCl_2$, into an alkaline solution of sodium arsenate, Na_2HAsO_4:

$$3CaCl_2 + 2Na_2HAsO_4 = Ca_3(AsO_4)_2 + 4NaCl + 2HCl;$$
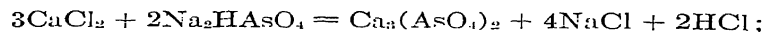
the hydrochloric acid is removed by the alkali in the sodium arsenate solution. The calcium arsenate is insoluble; it precipitates and is filter-pressed and shipped as a paste or dried to a powder.

Calcium arsenate may be substituted for lead arsenate, except in treating trees with tender foliage; it is more injurious than the lead arsenate; it is less adhesive, but this may be remedied by using it in conjunction with Bordeaux mixture, or with lime. The great advantage of calcium arsenate is its low price,[9] which has permitted among other things its use in the cotton fields for the destruction of the dreaded boll weevil. Calcium arsenate has been found a superior insecticide for

[7] U. S. Patent 1,417,232.
[8] U. S. Patent 1,175,565.
[9] Calcium arsenate 6.75c; lead arsenate 11.5c; Paris green 22c (1937).

this pest, and the general method of application is as a dust, without dilution.[10]

Even at 6.72 cents, calcium arsenate is too dear for its general use in the cotton fields against the boll weevil. Dilution would not do, but a method of preparation has been found by means of which an inert kernel of calcium carbonate is coated by calcium arsenate, the resulting powder remaining as effective as the pure calcium arsenate. This important contribution is from the Chemical Warfare Service Boll Weevil Investigation Board, and is an example of the peace-time functions of this bureau. Mixtures of precipitated chalk and white arsenic are heated
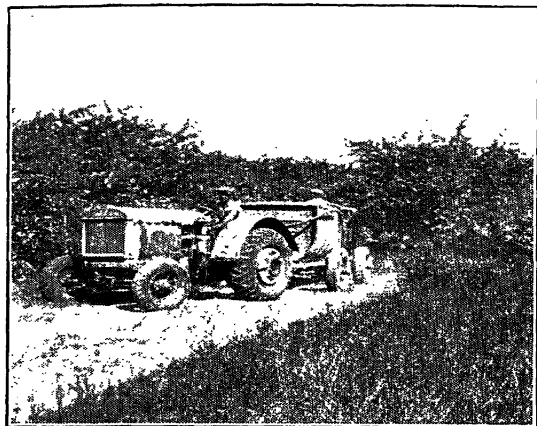
FIGURE 190a.—The full-size sprayer assembly consists of a tractor, and the spray tank with a small pump for the liquid and a blower. Pump and blower are operated by a separate gasoline engine. Dry dust is applied with very similar apparatus. (Apple orchard, Cobblestone Fruit Farm, Sodus, N. Y.)
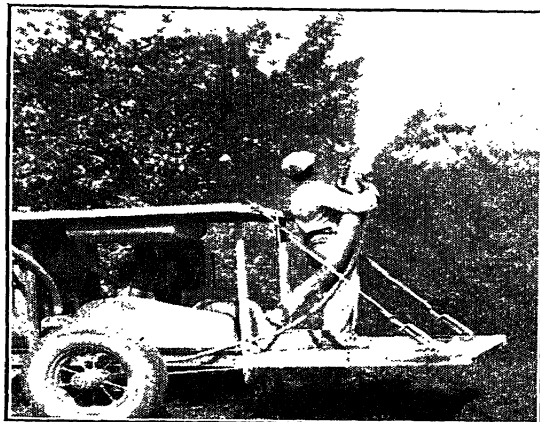
FIGURE 190b.—The lime sulfur solution is atomized in the nozzle and the rich mist directed into the tree. Pump for the liquid is at left; the blower is just behind the operator. (S p r a y i n g McIntosh apple trees, Sodus. N. Y.)

with excess air at 650° C.; the arsenic is changed to the pentavalent form, as normal tricalcium arsenate. It has been established that this material, with only 24 per cent As_2O_5, is as effective against the boll weevil as the ordinary calcium arsenate, with 40 per cent AsO_5.

In spray form, the proportions recommended for both lead arsenate and calcium arsenate are 1 pound of the powder to 50 gallons of water (about 0.25 per cent). The method of spraying trees in orchards requires two operators; a gasoline-driven pump and a tank are placed on a flat-topped wagon; one man guides the horses or the tractor, the other directs the spray.

[10] "The principles of insect control," Wardle and Buckle, Manchester, University Press, 1923, p. 90.

Paris green is used less now than formerly, because its injurious effects on the foliage is greater than that of lead arsenate, which has replaced it to a considerable extent. Furthermore, the adhesiveness is poor and the price high. It is still used in appreciable quantities, however; many farmers consider it the most effective remedy for the potato bug. The method of manufacture is to add a solution of copper acetate to a solution of arsenious acid, H_3AsO_3; there is precipitated a copper acetoarsenite of indefinite composition. This is filter-pressed and dried. Paris green has a higher tolerance for water-soluble arsenic than lead arsenate; it must not exceed $3\frac{1}{2}$ per cent As_2O_3.

Hellebore is the powdered root of the hellebore plant, *veratrum album;* it contains alkaloids which poison the insect but, in the small quantities used, do not affect man. When applied dry, the powder is diluted by mixing it with flour or lime; when applied wet, the dilution is by the water used. Hellebore has the advantage that it may be applied to crops soon to be eaten, so that arsenicals would be inadvisable; it serves only for restricted areas, such as gardens and truck farms.[11]

The Contact Insecticides. The contact insecticides are effective against the boring insects which have soft bodies, such as scale insects, plant lice, pear thrip, red bug, red spider, and others. By means of these chemicals, the insects are poisoned, paralyzed, or, killed by covering the skin with a film of oil which closes the breathing pores. Lime-sulfur, nicotine, soap solutions, kerosene, and oil emulsions are the important members of this group.

Lime-sulfur is used both in solution, as a spray, and in the dry powder form, as a dust. It is manufactured by boiling sulfur in milk of lime, with the formation of calcium polysulfide and small amounts of a number of sulfur compounds of no importance. The solution is yellowish-brown; after filter-pressing or decanting the clear liquor, it is concentrated to 32° Bé. cold, when it contains about 24 per cent of sulfur in solution. This solution is shipped in tight oak barrels, and is diluted with 8 parts of water for the San José scale, 16 parts for the peach leaf curl, 42 parts for apple tree spray, and 54 parts for pear and cherry trees.[12] There is also in wide use a home-made lime-sulfur solution, which has the same composition and effectiveness as the commercial material. Lime-sulfur is also sold in the dried form, and this may be applied as a dust.

Nicotine in the form of nicotine sulfate is made from refuse tobacco and is sold as a 40 per cent solution. This is diluted so that the spraying liquor contains not less than 0.06 per cent nicotine; it is advisable to dilute in a soap solution, which acts as a spreader, containing 2 pounds

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[11] Fluosilicates have been introduced as insecticides; *see* Chapter 3 for their manufacture, and "The fluosilicates as insecticides," S. Marcovitch, *Ind. Eng. Chem.*, **18**, 572 (1926).

[12] "Injurious Insect Pests and Fungous Diseases," reference 1, p. 59.

of soap to 50 gallons of water. A satisfactory nicotine extract may also be home-made, by steeping stems and sweepings of dried tobacco in water at ordinary temperature. If refuse tobacco is purchased, the cost is reduced inasmuch as the extracted material is a good fertilizer. The strength of the extract is fixed by using definite weights of tobacco, and consulting the table furnished by the United States Department of Agriculture.[13] Such home-made extracts contain the nicotine in the form of the free base; the commercial, concentrated extract is the sulfate of nicotine because the free base is volatile and would be lost during concentration, while the sulfate is fixed.

Nicotine powder is made by pulverizing stems, and may contain very little nicotine. The strong extract may be applied in the form of a dust by mixing it with gypsum, kaolin, or hydrated lime, or a mixture of these; the choice of the added solid has a definite influence upon the effectiveness of the dust.

Soap solutions are usually fish-oil soaps, containing 1 pound of soap to 4 gallons of water or more; the strength depends on the kind of insect to be destroyed. Fish-oil soap solutions are efficient against plant lice. The soap solution is frequently used with nicotine solutions, arsenate of lead and Bordeaux mixture. The soap may be purchased, and may be a potassium or sodium soap, preferably the former; it may home-made from fish oil and lye; in either case, the soap retains a strong fish-like odor.[14]

Kerosene, crude oil, and lately lubricating oil emulsions have been used with success. A kerosene oil emulsion may be made as follows: one-half pound of fish-oil soap is dissolved in 1 gallon of water, and 2 gallons of kerosene added to the hot solution; by pumping it back and forth, or by violent agitation, a creamy emulsion forms which on cooling does not separate. For use on dormant trees, the dilution is 1 part to 7 of water.[15] Other emulsions are made in a similar way.

Miscible oil emulsions are made by mixing an emulsifying solution containing fish-oil soap, carbolic acid and kerosene, with the "miscible oils," paraffin oil (28° Bé.) and rosin oil.[16]

Pyrethrum and rotenone either in powder or as the extract are widely used as horticultural and household insecticides.

Insecticides in Vapor and Gas Form. Stored wheat and other grains are subject to insect pests which are readily destroyed by pouring carbon disulfide on the grain and closing all outlets; such fumigations are practicable only when the material is contained in a building which can be closed hermetically during treatment. Carbon disulfide and air mixtures are explosive; to avoid this danger, there has been developed a

[13] *U. S. Dept. Agr., Farmers' Bull.* **No. 908,** 41 (1920).
[14] *U. S. Dept. Agr., Farmers' Bull.* **No. 908,** 36 (1920).
[15] "Injurious Insect Pests, etc.," reference 1, p. 55.
[16] *U. S. Dept. Agr. Farmers' Bull.* **No. 908,** 32 (1920).

new fumigant, a mixture of ethyl acetate and carbon tetrachloride which is non-explosive, vaporizes almost as readily, and is nearly as efficient.

Hydrocyanic acid, HCN, is an excellent fumigant, and although a deadly poison to man, may be handled safely. A dish containing the proper amount of sodium cyanide is placed underneath a bottle containing sulfuric acid, which can be upset from near the door by an arrangement of strings and small pulleys. As the operator is about to step out, he pulls the string and closes the door. This gas is applied to citrus trees in California, by placing over the tree a cotton duck bag which reaches to the ground; the gas is generated by acid on sodium cyanide and destroys the insects without hurting the tree. Calcium cyanide is also used.

Carboxide is the trade name for a mixture of 1 part ethylene oxide and 9 parts carbon dioxide, a safe and effective fumigant; it is non-flammable and non-explosive. It is obtainable compressed to a liquid in steel cylinder; the material issues from the cylinder in a fine spray or mist which vaporizes immediately.

The peach borer works near the ground and cannot be reached by sprays or dusts; para-dichlorobenzene, a solid, placed in a small trench around the base of the tree, destroys it.

FUNGICIDES

The fungous diseases which attack the fruit-trees, vines, and farm crops are perhaps more serious even than the insect pests, because once the fungus has grown, it is so tough that it resists chemicals; it is only while the spores are young and tender that they can be destroyed with surety. The work against fungous diseases thus takes on the aspect of prevention rather than cure; in keeping with this policy, nursery stocks and seeds are fumigated [17] and dipped before sale.

Some of the fungous diseases are mildews, apple and other scabs, rust. leaf spot, brown rot of plum and peach, and bark cankers. The important fungicides are sulfur, Bordeaux mixture, lime-sulfur, already listed as a contact insecticide, formaldehyde, corrosive sublimate ($HgCl_2$), and a number of organo-mercuric compounds.[18]

Sulfur, in the form of a fine powder under the names of dusting sulfur (99 per cent S), sulfo-dust, dry mix (61 per cent S) and other names. is applied mainly as a dust, in a few cases as a suspension in water or better, soap solution. It is estimated that in Europe over 100,000 tons of powdered sulfur or flowers of sulfur (sublimed) are used every year against the microscopic fungus *oidium*, which causes the grape vine leaf to dry.

[17] Example. the dust Semesan (Dupont) containing 35 per cent hydroxymercuriphenol, applied to the seeds, destroys fungi (which include molds and bacteria).

[18] "The manufacture of sulfuric acid in the United States." Wells and Fogg, *Dept. Interior Bull. No. 184*, p. 27; see also *Ind. Eng. Chem.*, **4**, 136, 140, 143 (1912).

The main sources of sulfur are Sicily and the Louisiana and Texas deposits; sulfur occurs in many other places, however, such as Japan, Mexico, and in the state of Wyoming. In Sicily, the sulfur occurs mixed with marl and gypsum; it is purified by heating and draining or running off the liquid sulfur; the fuel is sulfur. In the coastal plain of the Gulf of Mexico, a strip of land 225 miles wide is sulfur-bearing; it lies partly in Louisiana, and partly in Texas. The sulfur lies at depths of 600 to 1100 feet, and the deposits average 125 feet. It is lifted from deposits between 600 and 2000 feet to the surface, by means of the Frasch process. The sulfur pocket must be covered by a fairly thick and tight cap, for the superheated water must be kept under 100 pounds gage pressure, in order to retain for it the temperature of 340° F. (171° C.). The heated water is forced down 6-inch casings into the deposit; the melted sulfur [melting point 112.8° C. (235° F.)] is forced upward through a 3-inch casing strung inside the outer 6-inch one. A 1-inch pipe inside the 3-inch one carries compressed air (500 pounds) to the liquefied sulfur and, mixing with it, divides it into gullets separated by the air, which make a column easier to lift. Not only must sulfur be located, but other conditions must be met before the mining of a given deposit can become a reality. For the production of 1000 tons per day, 2 to 3 million gallons of water are required, a 4000-horsepower boiler plant, fuel, pipe lines and bins for receiving the liquid sulfur, and the possible necessity of disposing of "bleed" water from non-producing wells in the same dome.[19] Continuous operation in the Frasch process is essential, for, if interrupted, the liquefied sulfur in the formation congeals and "freezes" the pipes in each hole.

The main uses of sulfur are for a fungicide as such, for making lime-sulfur, for the sulfite pulp process in paper-making, for manufacturing sulfuric acid (supplementing pyrite), for vulcanizing rubber, and for the manufacture of carbon disulfide.

The production in the United States in 1935 of sulfur as brimstone, mainly Texas and Louisiana brimstone, was 1,632,590 tons; in 1936, 2,011,391 long tons. The peak was 1930, when 2,558,981 long tons were mined.

Bordeaux mixture is probably the most important fungicide used in the United States; it may be purchased in the form of a powder and made up with water, or it may be home-made. It consists of copper sulfate and lime, and for the home-made spray, ready to apply to the crops, the proportions are as follows:[20] 4 pounds of copper sulfate $CuSO_4 . 5H_2O$, called bluestone, are dissolved in 25 gallons of water; 4 pounds of fresh stone lime, or quicklime (CaO), are dissolved in 25 gallons of water, and the two solutions are mixed, in the spray tank itself for example. The concentration is correct for summer spraying; a little

[19] J. H. Pollard, *Chem. Met. Eng.*, **39**, 394 (1932).
[20] *U. S. Dept. Agr., Farmers' Bull.* **No. 908**, 39 (1920).

less bluestone is taken for spring spraying. This mixture gives a bluish deposit, which on the green leaves is very noticeable.[21]

Formaldehyde solutions are used to prevent potato scab, oat smut, the stinking smut of wheat, and onion smut. The method for potatoes is to place the seed potatoes in a solution containing 1 pint of 40 per cent formaldehyde solution (CHOH) in 30 gallons of water, for two hours. The oats may be spread on the floor and the solution poured on them. Other uses and the method of manufacture of formaldehyde will be found in Chapter 35.

Mixed Sprays and Mixed Dusts. It is often desirable to apply two chemicals or even three at the same time, in order to save labor; an insecticide and a fungicide may be mixed, since insects and fungous disease often occur together. Mixed sprays are widely used; thus lime-sulfur, arsenate of lead, and nicotine sulfate may be used together; the same three materials may be used as a dust. Bordeaux mixture, arsenate of lead, and nicotine is another suitable combination. A circular diagram (Fig. 191) indicating the proper choice is given in several government publications and in farm journals.[22] Certain combinations are incompatible, and must be avoided; thus soap solutions must not be used with lime-sulfur.

DISINFECTANTS

The chemical industries perform an important service in furnishing disinfectants which supplement sterilization by steam or flame. The function of a disinfectant is to kill bacteria and to prevent further growth of new cultures. A germicide also kills bacteria, but its power to prevent further growth is secondary; an antiseptic inhibits bacterial growth without necessarily killing.

Among the important chemical disinfectants are: phenol, cresol, guaiacol, thymol, formaldehyde, potassium permanganate, bleaching powder, calcium hypochlorite, sodium hypochlorite, chlorine, bichloride of mercury, aristol, hydrogen peroxide, mercurial phenols. The standard is a 5 per cent phenol solution; the power of other substances is expressed in terms of the standard, and this value is known as the phenol coefficient. The method is to make a bacterial count before and after application. The phenol number varies with different bacteria.

The Carrel-Dakin solution,[23] discovered during the war, would be classed as an antiseptic; it consists of a 0.5 per cent sodium hypochlorite solution, made from bleaching powder, just alkaline. It is used to irri-

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[21] The discovery of the fungicidal value of Bordeaux mixture was accidental; while walking in a vineyard, the French scientist Millardet noticed that the vines at the edge of the vineyard had not lost their leaves while the rest had; the custom was to spray the edges with a mixture of copper sulfate and lime in order to scare off thieves who mistook the bluish deposit for poison (1882). This led to experiments by Millardet and Gayon, which established the value of the same mixture as a fungicide.

[22] *U. S Dept. Agr., Farmers' Bull.* **No. 908, 73** (1920). "The principles of insect control," Wardle and Buckle, p. 116. *See* reading references. A highly esteemed farm journal is the *Rural New-Yorker,* published at 333 West 30th Street, New York.

[23] U. S. Pharmacopœia, **10th ed.** (1926).

gate wounds, so that the dead tissue is dissolved, thereby removing the food of bacteria, which die as a consequence.

Barium carbonate is a rat poison, harmless to dogs.
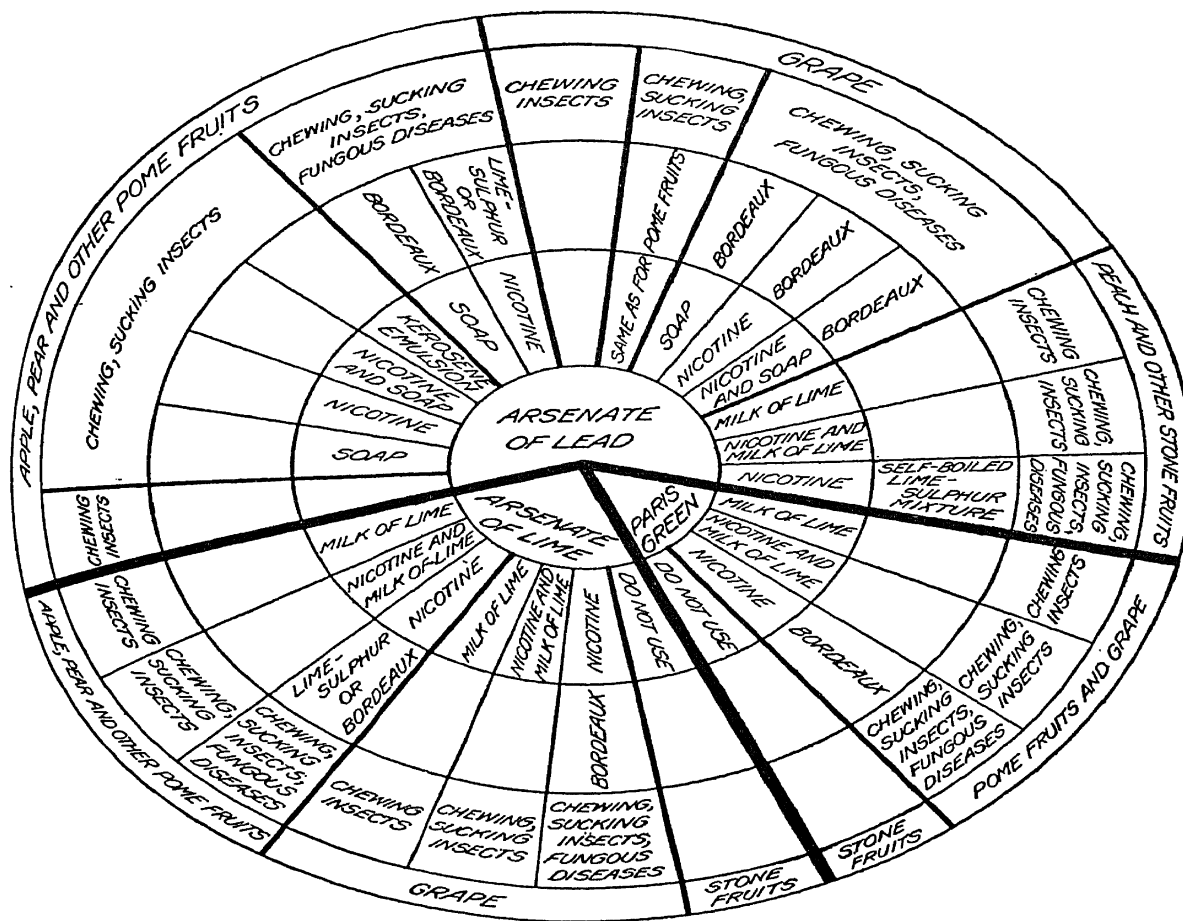
FIGURE 191.—Chemicals which may be used mixed together, so as to allow treatment for two or more diseases. Only the chemicals within heavy lines may be mixed. (From *U. S. Dept. Agr., Farmers' Bull.* No. 908.)

A 1 to 1000 water solution of hexylresorcinol (n-hexyl-2,4-dihydroxy-benzene) kills bacteria in 15 seconds; it has a low surface tension, which permits its penetration into small spaces, an important advantage. It is non-poisonous.

WOOD PRESERVATION

The preservation of wood for railroad ties, fence posts, and in general of all wood used outdoors is an important problem. In the past, treating

with creosote oil (see Chapter 14) has been the chief method, and remains an excellent one. The practice is to heat the wood in order to drive out moisture and air, apply a vacuum to the containing chamber in order to free the pores of the wood, and sending in hot creosote, under gradually rising pressure.

In the year 1935, the creosote oil importations were 34,513,486 gallons, valued at $3,536,500. Creosote oil comes in free of duty. In addition, there were produced domestically in that year, 92,869,152 gallons of the same oil (10.2 cents a gallon). Essentially all this oil is for wood preservation.

Another chemical agent used for treating lumber for its preservation is zinc chloride; over 20 million pounds are used for this purpose in a normal year.

The preserving of wood for marine purposes is a specially vital problem. In certain infected areas, the shipworm causes untold damage in a short time. The *Teredo navalis* and the *Bankia gouldi* are the two best-studied examples of the shipworms. They bore into the wood of piling or ship-bottom and in a short time honeycomb it with burrows so that the wood collapses. The marine piling investigation [24] conducted by the Chemical Warfare Service has shown in a preliminary way that certain of the war gases, best dissolved in creosote, would be superior agents for marine preservation.

OTHER PATENTS

U. S. Patent 2,064,728 and 2,060,311, making colloidal sulfur; 2,044,214, sulfur refining process; 2,046,546-7-8, process for removal of insecticidal residues from fruits and vegetables; 1,928,968, colloidal dispersions of rotenone by the aid of tannic acid; 1,884,542, preparation of arsenical compounds suitable for use as insecticides; 1,875,466, esters of the fatty acids derived from animal or vegetable fats or oils are insecticidal and non-injurious to plant life; 1,877,851, an insecticidal containing petroleum oil, a compound of nicotine with an oil-soluble sulfonic acid derived from petroleum and an emulsifying agent; 1,842,443 and 1,863,519, an insecticide containing aluminum sulfate, potassium hydroxide, and hydrofluoric acid; 1,849,778, a fungicidal distilling composition containing a complex copper salt of mercury thiocyanic acid; 1,890,774, a dust disinfectant, from mercuric chloride, chlorophenol, sodium carbonate and hydrated lime; 1,801,144, disinfectant using 500 parts hydrated lime, 200 parts water, 50 parts mercury acetate; 1,791,430, a fungicide and bactericide consisting of zinc sulfate and lime.

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If the many goods made of rubber were suddenly removed from our economic life, a serious disturbance would be caused. Rubber belts drive machinery, rubber hose protects property from fire, rubber heels add to the comfort of the body, rubber tires have been a major factor in the rapid growth of the automobile industry. The plight of Germany during the late war when its importation of crude rubber was stopped is an indication of how serious the disturbance would be.

Chapter 39 *

Rubber

The hydrocarbon, rubber, $(C_5H_8)_x$, is found in many plants, trees and shrubs. Over 98 per cent of the world's supply however comes from the rubber tree, *Hevea brasiliensis*, and 97 per cent from cultivated plantations of this tree, mostly in Ceylon, British Malaya and the Dutch East Indies. Other sources such as guayule, goldenrod, etc., are difficult to utilize commercially on account of the large amounts of resins and other substances associated with the rubber.

In a primitive form, rubber has been known in America for centuries; archeological records in Honduras dating back to the 11th century show the use of solid rubber balls in native games, and early Spanish explorers mention the use of rubber latex to coat cloth and render it waterproof. In Europe, the house of James Lyne Hancock, Ltd., London, was established in 1820, and claims to be the oldest rubber factory in the world. Modern rubber products, however, did not begin to appear until 1839 when vulcanization,[1] the reaction of sulfur with rubber to produce a chemical and physical change, was discovered by Charles Goodyear, and a factory started at Springfield, Massachusetts, in 1841. By 1876, the manufacture of raincoats, carriage tires and other rubber articles was a thriving little business, rubber coming from the Amazon region in Brazil, where it was gathered by natives from wild trees in the tropical forests. Henry Wickham, British explorer, visioned the future growth of the industry and the necessity of cultivated plantations of rubber trees to assure a steady source of supply. He determined to make the industry independent of the Brazilian monopoly, and succeeded in smuggling 70,000 seeds of the *Hevea brasiliensis* out of Brazil. The seeds were raised at the Kew Gardens in London, only 4 per cent reaching the plant stage; the seedling trees obtained were transported to Ceylon. From this start has come our rubber industry, to supply which, plantations in 1935 covered over 7,000,000 acres and produced 844,554 long tons of rubber. The

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* In close collaboration with Mr. Raymond B. Stringfield, Consulting Chemical Engineer, Los Angeles, California.

[1] The credit for the discovery of vulcanization should be granted to four individuals, in equal measure, Dr. F. W. Luedersdorff (1832), Nathaniel Hayward [U. S. Patent 1090, (1839)], both of whom discovered the beneficial action of sulfur, Charles Goodyear [U. S. Patent 3633, (1844], and Thomas Hancock (in England), who both discovered the importance of heat in sulfur vulcanization. [From the Vanderbilt (1936) Rubber Handbook, p. 111].

best buyers were the United States, with imports of 455,758 long tons in 1935.

The rubber producing countries of the world, in the order of the 1934 production, are as follows: British Malaya, 467,000 long tons; Netherlands Indies 380,000; Ceylon 79,000; British Borneo 29,000; French Indo-China 20,000; Siam 18,000; British India 12,000; Brazil 9,000; others 5,000.

Plantation Production. A plantation is divided in quadrants; one quadrant is worked for a year, then is given three years' rest. The trees begin to yield latex when they are six years old, and continue till over forty. The size of the full-grown rubber tree is about that of the maple. In the *Hevea brasiliensis*, rubber ocurs as a milky latex in a series of vessels just under the bark. Native tappers remove a shaving of bark from a diagonal cut extending one-third around the tree, and collect in small cups the latex which flows out. Trees may be tapped daily or every other day. About ¼ of a pound of latex is the daily yield of one tree. The latex, which averages about 35 per cent rubber, in the form of particles 1 to 2 μ in diameter dispersed in a watery serum, is brought to a collecting station, diluted to about 15 per cent rubber content, and coagulated by addition of acetic or formic acid.[2]

The bulk of the rubber comes on the market as *ribbed smoked sheet*. This is made by sheeting the coagulated rubber on even-speed rolls with light washing, and drying from 7 to 11 days at 40 to 50° C. (104-122° F.) in an atmosphere of smoke from burning fresh wood.[3] The smoke turns the rubber brown, and acts as a preservative, preventing the development of mold in the serum substances remaining in the rubber. The smoked sheets are pressed into square bales of 200 to 220 pounds, and protected with plywood for shipment.

Another important grade of rubber is *pale crêpe*. For this, sodium bisulfite is added to the latex before coagulation, and the coagulum washed thoroughly on differential-speed rolls to tear the rubber apart and remove serum substances. The sheets are then dried without smoking, yielding a yellowish-white rubber which is baled as before. Other lower grades as brown crêpe, blanket crêpe, rolled brown and plain unsmoked sheets are made by various plantations.

Due to variations of supply and demand and other economic conditions, the price of rubber has varied considerably in recent years, as shown in the table below:

TABLE 72.—*Range of Rubber Prices, Cents Per Pound. (Smoked Sheets and Crêpe.)*
(*From the "Annalist."*)

1929	21¾ to 20⅝	1933	7¼ to 3¹¹₁₆
1930	15⅞ to 9¼	1934	16⅝ to 10
1931	8¼ to 5⁷₁₆	1936	12⅝ to 11¹¹₁₆
1932	5 to 3⅝	1937 to May 1st	25⅝ to 20⁹₁₆

[2] The rubber latex particles exhibit a lively Brownian movement under the ultra-microscope. The particles are spherical in the latex from young trees, slightly egg-shaped if from older trees. Each particle contains a drop of oil, which is in a sack made of the same oil but gelatinized, and the whole is stabilized by casein.

[3] The name of the plantation is embossed in the sheet.

Vulcanization. Raw rubber has few commercial uses as it softens when heated, freezes when cooled, is soluble in coal tar or petroleum solvents, is plastic, tacky, and has low tensile and other unsatisfactory physical properties. By mixing with sulfur, in the form of flowers of sulfur, a fine powder, usually not over 3 per cent on the rubber, and heating, a change called vulcanization takes place, part of the sulfur combining chemically with the rubber hydrocarbon, and changing its physical properties so that it is no longer affected by ordinary temperature changes, is swelled but not dissolved by solvents, and has greatly increased tensile, abrasion resistance, etc. Vulcanization may be carried out in various ways: in hot water or air (as with rubber gloves), in an autoclave with steam (as with rolls of rubberized fabric), or in molds heated with steam (as with tires) or heated by the platens of a hydraulic press (as with heels and most other articles).

Vulcanization is a progressive reaction; it should be allowed to progress to a definite point, and not beyond. Rubber which has not been heated long enough is said to be "undercured," while rubber which has been heated too long may be "overcured."

With sulfur and rubber alone, approximately 120 min. at 287° F. (141.7° C.) is required to accomplish vulcanization. In recent years, *accelerators* have been developed which greatly speed up this process. A few inorganic compounds as litharge, lime and magnesium oxide have accelerating action, but have been almost entirely replaced by more powerful organic compounds. These are used in amounts varying from 0.1 to 1.5 per cent, and certain combinations can reduce the time of "cure" or vulcanization to as little as 3 min. at 200° F. (93.3° C.) Commonly used as accelerators are mercaptobenzothiazole, (captax), C_6H_4 . $N:C(S)SH$; diphenylguanidine, (DPG), $(C_6H_5NH_2)_2C:NH$; tetramethylthiuramdisulfide, (tuads), $(CH_3)_2NCS . S . S . CSN(CH_3)_2$; and zinc dimethyldithiocarbamate, (zimate), $[(CH_3)_2NCS . S]_2Zn$.

Vulcanized rubber deteriorates from oxidation, particularly if exposed to sunlight. Chemicals which retard this deterioration have been developed and are widely used. These are usually called *antioxidants,* and 1 per cent is sufficient to greatly increase the life of the rubber product. Commonly used antioxidants are aldolalphanaphthylamine and phenyl betanapthylamine.

Compounding, compounding ingredients, and reasons for their selection. The whole art of mixing other ingredients with rubber and of processing the mixed compound to control its physical properties, both before and after vulcanization, is called *compounding.* The use of *sulfur, accelerators* and *antioxidants* has already been mentioned. Other materials are used for *accelerator activators, accelerator retarders, rubber substitutes, softeners, stiffeners, odorants, fillers*[4] and *pigments.*

[4] For comparison purposes, it is customary to calculate all formulae for rubber compounds in per cent by weight on the weight of the rubber present, or in volumes of filler per 100 volumes of rubber. The latter is particularly useful as it takes into account the specific gravity of the materials used. Thus rubber has a sp. gr. of .92, ZnO 5.57, and carbon black 1.80, and either 55.7 lbs. ZnO or 18.0 lbs. C would be a 10 vol. loading when mixed with 92 lbs. rubber.

Almost every rubber compound carries from 1 to 5 per cent zinc oxide and at least 1 per cent stearic acid or suitable substitute, their purpose being to activate the accelerator present and enable it to produce its full effect. Occasionally materials such as benzoic acid are added to retard the effect of the accelerator, particularly at low temperatures, so the compound will not cure prematurely during processing.

Rubber-like products called *factice* can be made by reaction of sulfur or sulfur chloride with vegetable oils, and find use in some soft rubber products such as erasers. Certain blown asphalts, known as *mineral rubber*, may be substituted for part of the rubber in stocks such as wire

	TIRE TREAD	GARDEN HOSE	INNER TUBE	TIRE CARCASS
PLANTATION RUBBER	100	100	100	100
RECLAIMED RUBBER	—	50	—	—
SULFUR	3	5	1.5	2.5
ACCELERATOR (TUADS)	—	—	0.1	—
" (CAPTAX)	1	0.25	1.5	1
ANTIOXIDANT	1	1	1	1
ZINC OXIDE	5	5	10	5
STEARIC ACID	4	—	2	1
SOFTENER	5	6	4	—
GAS BLACK	45	—	—	—
SOFT BLACK	—	25	40	—
CLAY	—	100	160.1	110.5
WHITING	—	100		
	164	392.25		
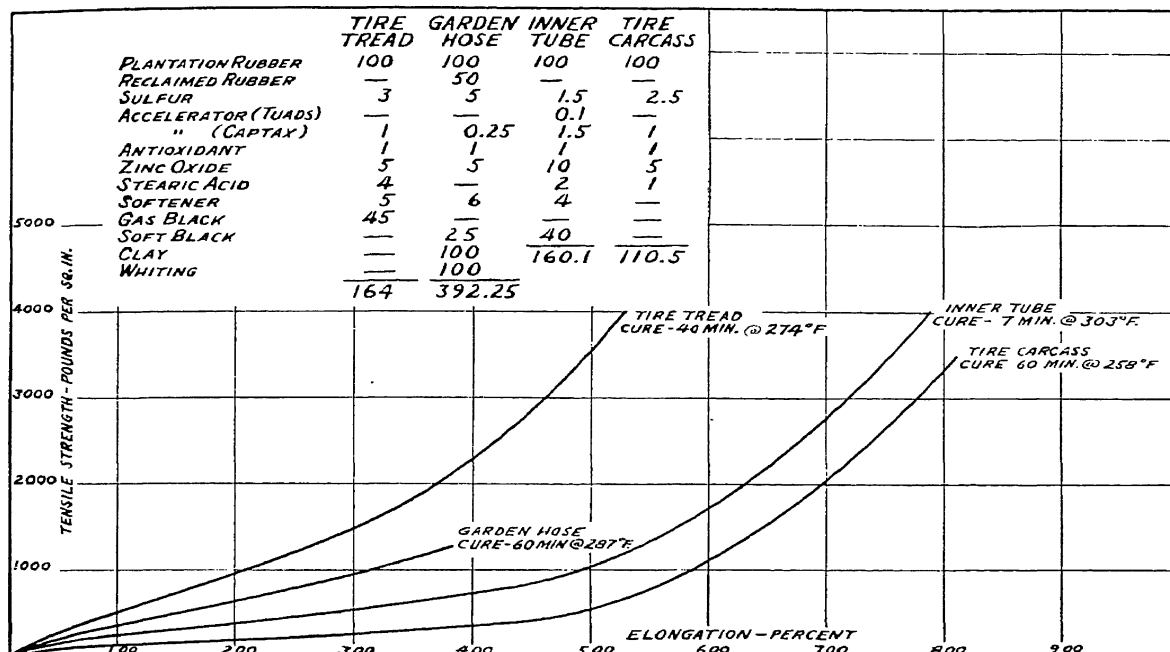
FIGURE 192.—A set of stress-strain curves of typical rubber stocks, a four formulæ for the compounding, all based on 100 parts of gum rubber or plantation rubber (crêpe or smoked sheets). [From the practice of Mr. Stringfield.] The reader will please note also the temperature and time of curing.

insulation where they aid the flow of the compound as it is extruded.

The mixing of the compounding chemicals is generally done at the mixing rolls, with the various materials added one by one in the selected order. Raw rubber is tough, and requires mastication on a mill until it is hot and plastic before other compounding ingredients can be added and the compound sheeted or shaped for the next operation. Softeners such as vegetable and mineral oils, waxes, tars, pitches and resins are added to save time and power and facilitate handling. Occasionally, particularly with highly compounded stocks, stiffening is desirable in the

uncured compound, and this can be accomplished by the addition of smal amounts of benzidine or p-aminophenol. For some household purposes the odor of rubber is undesirable, and odorants have been developed that in quantities as low as .25 per cent, persist through vulcanization and aid the sale of the product.

"Pure gum" products, that is, pure vulcanized rubber products, would be too soft and elastic for most commercial uses, so fillers are commonly added to the rubber; they increase the hardness, stiffness, tensile strength and resistance to cutting, tearing and abrasion. Their action is purely physical, and is due chiefly to their fine particle size and good dispersion in the rubber. The most important of these fillers is carbon black, made by the channel process; it is used in all articles which receive extremely rough service, such as tire treads, and conveyor belts. Zinc oxide is used when the stock must be light colored; it is not as effective as carbon black, and is much more expensive on a volume basis. Many other non-reinforcing fillers as whiting, clay, slate flour, may be used in certain places to add weight, stiffness, reduce elongation, improve processing or reduce costs. Such uses are entirely legitimate, there being no object for instance in having high abrasion resistance in a product not subjected to rough usage. Color pigments, dyes or lakes may be used where colored products are desired.

The compounding formulae for four typical rubber stocks, tire tread, garden hose, inner tube, and tire carcass are given, with a set of stress-strain curves for these same stocks after vulcanizing at the temperature and for the period given on the graph, Figure 192. In a vulcanized article, the ratio of combined sulfur to the rubber is called the *vulcanization coefficient* or VC. Of great value is also the ratio of accelerator to rubber.

Stock Preparation. The main operations in preparing rubber stock are *milling, calendering* and *extruding* or "tubing."[5] The rubber compound is milled for two purposes; first, to mix and thoroughly disperse the ingredients; and second, to plasticize the rubber and render it more adaptable to later operations. This is done on two types of equipment, mixing rolls and internal or Banbury mixers. For large production, mixing rolls are usually 84 inches long and 22 or 26 inches in diameter, and of cast steel about 5 inches thick, the inner surface being cooled with a spray of water. Two such rolls are mounted together horizontally, geared to revolve toward each other at a ratio of about 1.0:1.25 and a surface speed on the slow roll of 95 feet per minute. Rubber placed on the rolls is squeezed downward through the "bite," and allowed to sheet around the slow roll back into the excess or "bank" on top of the rolls. One roll is adjustable to vary the thickness of the sheet between $\frac{1}{8}$ and $1\frac{1}{4}$ inch. When the rubber is soft enough, the operator begins adding the other ingredients in proper order, "working" the batch, from time to time, by cutting the sheet on the roll to bring fresh material through the

[5] It was formerly necessary to *wash* and *dry* the raw rubber to remove sand, bark, etc., but plantation rubber is now so clean that this operation is usually omitted. For some special purposes, as for inner tubes, rubber may be *strained* by extruding through a fine screen.

"bite." A batch may vary from 50 to 350 lb. depending on its type, and may require from 10 to 60 minutes for milling. Approximately 100 H.P. are required for operation, most of which appears as heat in the rubber stock, which has to be rapidly removed by the cooling water to prevent premature vulcanization or "scorching." Even with this cooling, the stock is usually about 200° F. (93.3° C.), and when mixing is completed, is cut off in slabs about 3 feet square and dipped in a slurry of talc and water to cool and prevent sticking together. Similar mills are used for sheeting out stock from Banbury mixers, and for "warming up" stock for calenders and tubers.

The Banbury mixer is an enclosed machine with two water-cooled mixing rotors operating in a water-cooled chamber. Mixing is very rapid, for example: an 84-inch mill will mix a 350-pound batch of tread stock in 30 minutes, while a number 11 Banbury will handle 650 pounds of the same stock in 18 minutes, or 3.11 times faster. The Banbury stock will also require an 84-inch mill to sheet out and batch off the mixed stock.[6] With the use of suitable compounds, mixing in a Banbury mixer results in a large saving of power. Several sizes are available, taking batches up to 650 pounds.

FIGURE 193.—Scheme for coating fabric with rubber on the calendering machine.
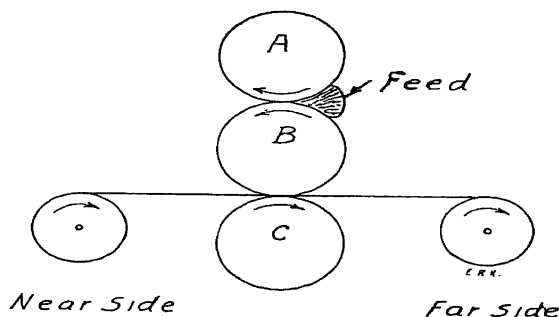
Calenders are usually 3-roll machines (Fig. 193) and are used for three general types of work, *frictioning, skim-coating* and *sheeting.* Cotton fabric is "frictioned" by passing it over roll C with roll B running at a higher speed, resulting in wiping the rubber compound into the voids in the fabric. Skimcoating is a similar operation but with roll B at the same speed as C so that a film of rubber is pressed into the fabric. For sheeting, roll C is lowered and a cotton "liner" used, the sheet of rubber formed between A and B being led into the liner in which it is wrapped. By placing rotary knives against the near side of B, strips may be cut of any desired width and rolled up in the liner passing over C, the excess rubber between the strips returning to the feed.

The extruding machine or "tuber" is essentially a steel cylinder con-

[6] Generally speaking, a Banbury mixed stock is usually somewhat tougher than the same stock mixed on a mill, and this gave originally a great deal of trouble, but modern compounding with the use of softeners has overcome the difficulty, and the practice of sending the stock to the tubers or calenders without allowing it to cool has effected large savings.

taining a close-fitting screw, which forces the rubber stock fed at one end out through a die at the other end, thus forming shapes such as treads, hose, inner tubes, etc. The tuber is jacketed to permit heating and cooling, and the extruded stock is usually cooled by passing through water.

Automobile Tires and Tubes. Approximately 80 per cent of all rubber grown is used in automobile tires and tubes. Fundamentally, an inner tube merely confines an air cushion, while the tire prevents the tube from expanding, protects it from abrasion and holds it on the wheel. Since they are the most important items of the rubber industry, tires and tubes deserve special mention.
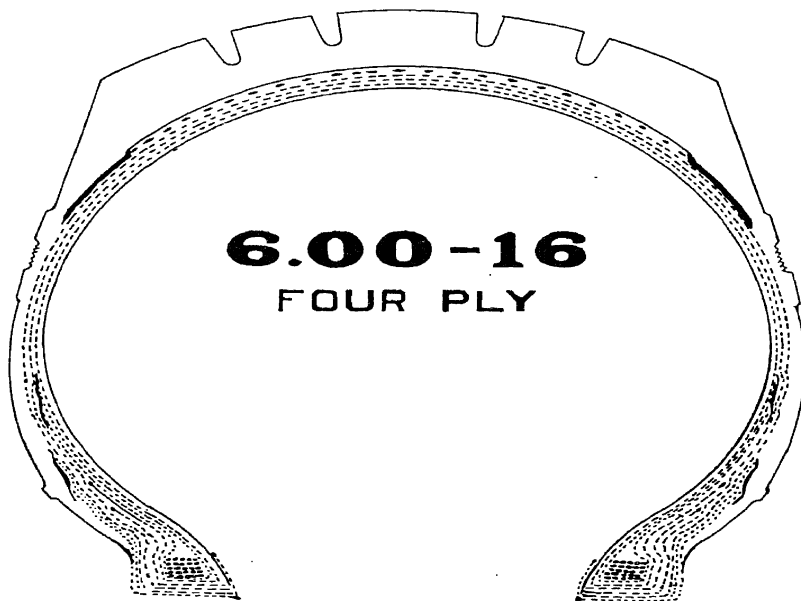
FIGURE 194. — Cross-section of a Dunlop 6.00-16 four-ply automobile cord tire for passenger cars. Note all the parts enumerated in the text, and designated in Figure 195. (Prepared especially for this edition by the technical staff, Mr. Howard Elden, Director, Dunlop Tire and Rubber Company, Buffalo, N. Y.)

At 60 miles an hour, the ordinary tire is flexing some 12 times per second, and the automobile engine is putting one-third of its power into heating the tires. The only construction that has been found to give reasonable service under such conditions is that of cord fabric, that is, fabric of heavy twisted cords with very few light cross-threads or none at all (pickless), imbedded in fairly soft rubber. The cords are coated on both sides with rubber by calendering, cut on a bias angle of 45 to 55°, and built into a tire "carcass" on a drum or collapsible core. "Beads" of wire imbedded in hard rubber are attached at the edges of the fabric bands to give rigid anchorage to the rim of the wheel (Figure 195). "Flippers" and "chafing strips" used around the bead "tie-in" are of light square-woven fabric frictioned and coated with rubber. The top-center of the carcass is protected by "breaker strips" of open mesh (leno)

fabric or of cords heavily coated with rubber, and a slab of tough abrasion-resisting stock which will form the tread. The sides are protected with thin slabs or "sidewalls."

For years, cotton has been the only material found suitable for the cord fabric, but recently rayon cord [7] has been introduced, with the expectation that it will prove superior, particularly in hot service. Several rayon plants are now producing rayon cord (Rayotwist, Cordura) exclusively. A large Eastern tire manufacturer expects to employ the rayon cord for one-fourth his truck tire production in 1937, and for a greater proportion after that.

Figure 195.—Construction of a straight-side cord tire: *A*, the flipper or bead covering; *B*, the bands or plies; *C*, the chafing strip; *D*, the hard rubber bead with enclosed braided wire.
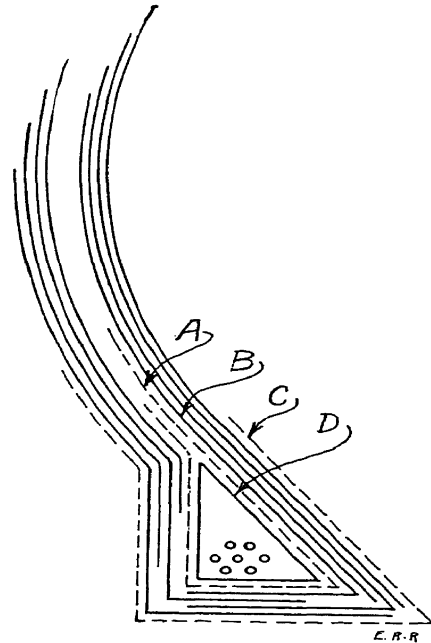
Passenger tires are built on a flat drum and shaped after removal by means of a vacuum chamber. Truck tires, being much thicker, are built on a collapsible core. After removal from the drum or core, the inside of the tire is coated with a non-sticky talc or mica composition, and an "airbag," resembling a very heavy inner tube, inserted. Steel rings, or "curing rims," are clamped to the tire at the bead to support the airbag at its inner side, and the tire placed in a two-piece cast iron or forged steel mold which has the lettering, numerals and tread design in inverse. This mold may be of the individual, or "watch case" type, having a jacket through which it is heated by steam, or it may be simply a movable mold of which 18 or 20 are stacked on a hydraulic ram inside an autoclave, where they can be held closed by the hydraulic pressure

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[7] *See* Chapter 22 for further remarks on the merits of rayon cord.

and heated by steam introduced around them. Air, and sometimes steam and hot water, are introduced into the airbag by flexible connections of copper tubing, expanding the tire carcass and causing the tread rubber to flow into the desired designs. The mold is then heated by steam for a specified time and temperature, such as 40 minutes at 307° F. (153° C.), to produce vulcanization. The steam is then shut off, the air released, the mold opened, the airbag removed and the tire sent to the final inspection.

Inner tubes were formerly cured on a steel or aluminum mandrel and spliced after curing, but now are usually spliced before curing and cured in a "watch-case" mold on pressure applied through the valve. The cure is very short, usually about 6 minutes.
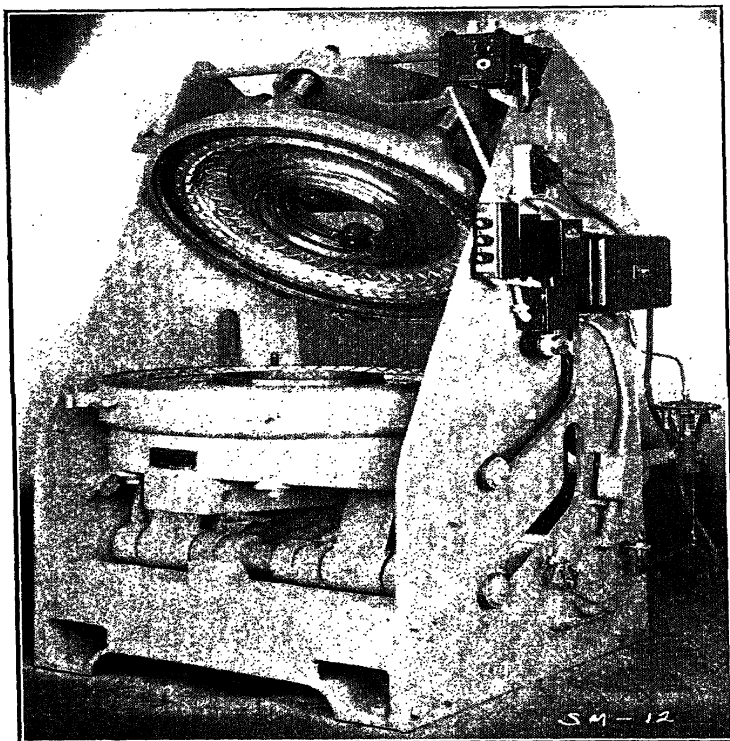
FIGURE 196.—An individual press of the latest design (1937) for curing automobile tires, also called a "watch case" mold. The castings are hollow to permit steam circulation. The mold opens automatically at the proper time. For inner tubes, the same type press is used, but with a smooth wall facing the rubber. (The Summit Mold and Machine Co., Akron, O.)

Rubber Belting. Rubber belting is of much industrial importance, both for driving machinery and for conveying materials. Coated fabric is folded as shown in Figure 197, adding layers until the desired thickness is reached. A sheet of cover stock, properly compounded to resist abrasion or other service, is then applied around the whole, and the belt cured in a flat press between steam-heated platens under hydraulic pressure

totaling usually not over 300 lbs. per sq. in. of belt in the press. Stretching devices are often used to keep the belt in tension during vulcanization.

Garden Hose. Seamless tubing of compounded rubber is extruded, and then passed through the center of a loom which weaves on a covering of threads. This, in turn, becomes the core for a second seamless rubber tube, second cover of cotton threads, and final cover of seamless tubing. This last then becomes the core for a seamless tube of lead, which is

FIGURE 197.—Arrangement of canvas plies in a rubber belt for driving conveyors (cross-section).
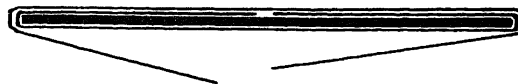
extruded by hydraulic pressure from a "lead press" carrying molten lead. The die through which the tube is passed is cooled so that the lead-covered hose emerges with the lead somewhat below its melting point. The hose is wound on a reel, placed in an autoclave, hydraulic pressure applied inside the hose, and steam introduced in the autoclave to produce vulcanization, after which pressure is released, the lead removed by a stripping machine, and the hose cut into lengths and couplings attached.

Rubber Heels. Stock for rubber heels is cut from sheets by means of a die, placed in molds and cured between steam-heated platens. The cure is usually about 15 minutes at 307° F. (153° C.). Tan heels are colored with red iron oxide. Heel stock contains considerable filler so that the heel can be properly buffed. To give some idea of the volume of this item, one plant is said to turn out regularly 300,000 pairs of heels per day.

Balata. This is a gum of importance in the rubber industry, for it is used in combination with rubber for golf balls. The crude balata is purified by solution in naphtha, filtration, and evaporation, yielding the wax-like, nearly white gum.

Tennis balls are made by hot pressing two hemispheres, then placing a pastille of ammonium nitrite inside, and cementing the two smoothed edges by a rubber cement, with heat. The ball is now sealed, and the nitrogen from the nitrite forms its inner gas. Two shaped pieces of felt are glued on for the covering.

Gaskets. Compounded rubber from the mixing rolls is cut to approximate circular size by means of very small, rapidly rotating knives; the knives are so thin that when whirling they are not visible. The rubber so cut is weighed and placed in the mold and cured. On removal from the mold the excess rubber is trimmed off by hand and the finished gasket of proper form and corrugations is ready for use. Small gaskets are stamped out.

Rubber Flooring. Flooring is usually made with a tiled effect. To produce this, squares or other shapes of the different colors are cut from semi-cured sheets, assembled to form the proper design, and placed over

a sheet of black rubber. The whole is then vulcanized under the usual pressure with steam heat to form a single piece of rubber, extremely durable and easy on the feet. Such flooring is used by the Pullman Co. and in many public buildings.

Hard Rubber. Most soft rubber articles contain only some three per cent of sulfur on the rubber. Between about 7 and 30 per cent sulfur is an intermediate zone in which the rubber products have little commercial value, due to stiffness, poor aging, etc. If 30 to 50 per cent sulfur is used, hard rubber results. Due to an exothermic reaction between the sulfur and rubber, thick articles of hard rubber have to be cured at low
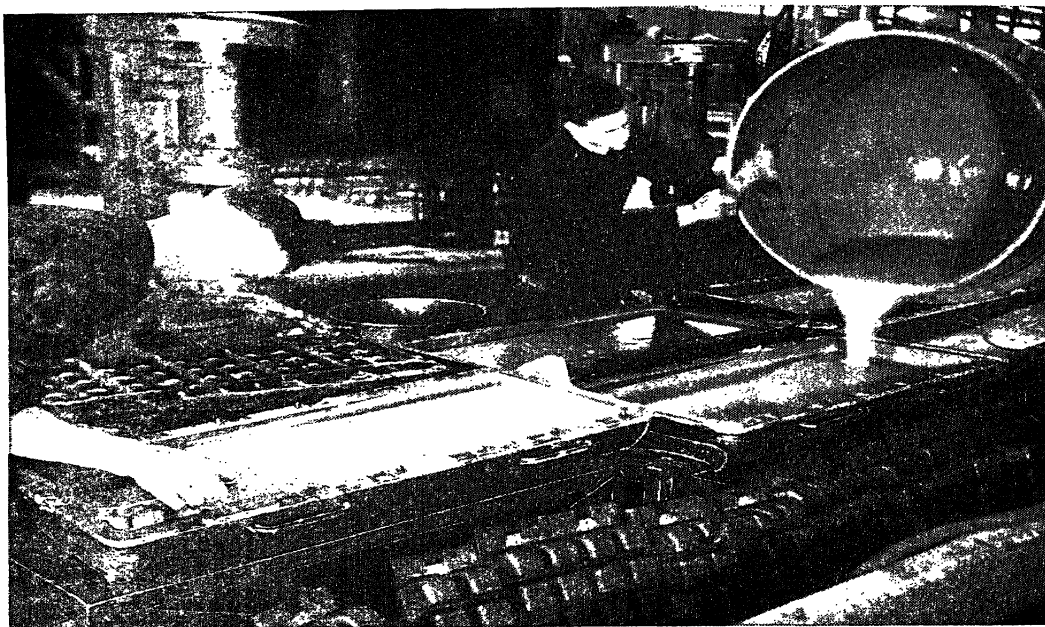
FIGURE 198.—Pouring compounded latex froth into molds during manufacture of cellular air cushions. (Courtesy of Dunlop Tire and Rubber Co.)

temperatures for long periods of time to prevent porosity or "blowing." Most hard rubber compounds contain lime or magnesia. Organic accelerators are useful in some small articles, but cannot reduce the time of cure to make it comparable with soft rubber. Hard rubber cures range from 30 minutes to 4 hours, and this makes the cost of curing much higher than that of similar articles made of synthetic resins, so that in this respect, hard rubber is at a disadvantage.

Cements and Doughs. An unvulcanized rubber compound can be swelled with gasoline or benzol, and by successive additions of solvent and working in a mixer, converted into a viscous dough or cement. Such cements are used to unite rubber surfaces in preparation for vulcaniza-

tion, and as adhesives for special uses. The thicker doughs are used to spread on, and thus coat with rubber, fabrics that are too light to stand calendering in the ordinary manner. Hospital sheeting and rubberized ginghams are made in this way, the coated fabric, after the solvent has evaporated, being rolled in a liner on a drum, protected with an outside rubber wrap, and cured in steam.

Latex. Rubber latex itself is now used in large quantities; it is shipped from the plantation to the consumer in drums, and even in tank steamers, after addition of ammonia to preserve and stabilize the emulsion. The raw latex may be concentrated by creaming, by centrifuging,
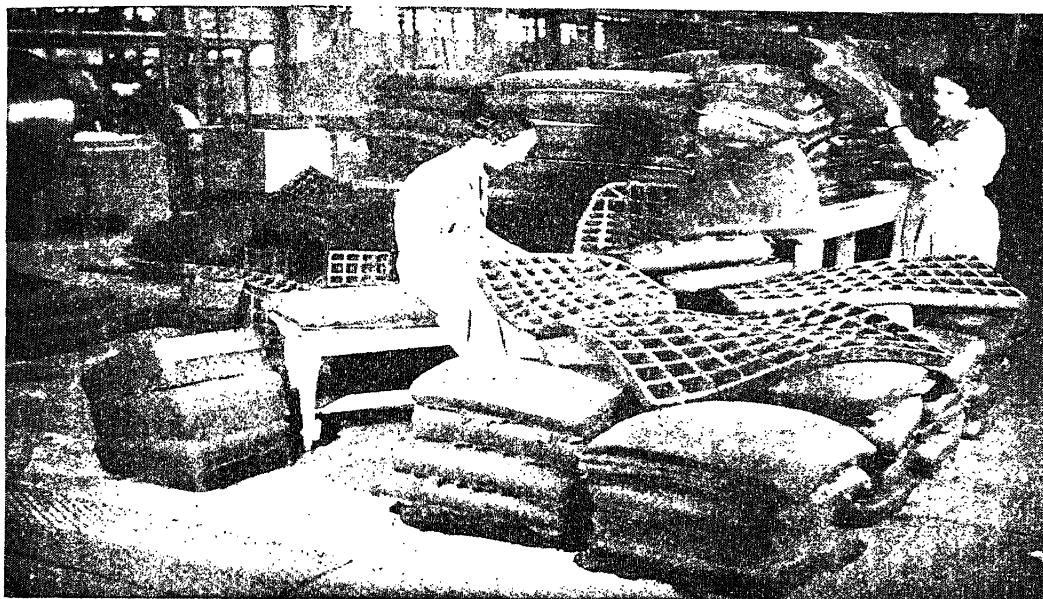
FIGURE 199.—Trimming vulcanized and dried cellular rubber cushions, made from latex. (Courtesy of Dunlop Tire and Rubber Co.)

or by evaporating part of the water after addition of a stabilizer, or in a vacuum. Sulfur, accelerators, and other compounding ingredients may be added by using proper protective colloids. Forms dipped in such compounded latex are used for making toy balloons, gloves and other thin objects. By making the form the anode, in an electrolyzing cell, thicker coatings may be deposited; the latex particle has a negative charge and separates out at the anode. Here also, the rubber deposit on the coated form is dried and cured in an air oven or a hot water bath.

To make the heavy rubber gloves used for protection in acid plants for instance, a porcelain form the shape of a hand is coated with calcium nitrate solution, and then dipped into compounded latex; a deposit forms of the exact shape of the hand; after it is thick enough, the form and

glove are plunged into warm water for curing. The finished glove may then be stripped off. The whole operation from beginning to end is a matter of minutes.

Sponge Rubber. Sponge rubber may be made by incorporating ammonium carbonate or stearic acid and sodium bicarbonate in a very soft rubber stock. The heat of vulcanization releases NH_3 and CO_2 which inflate the compound to a spongy mass, the size of the pores depending on the amount of gas, the softness of the stock and the rate of vulcanization.

Sponge is also made from latex, to which as been added a frothing agent (such as a castor oil soap) and into which subsequently air has been beaten. A slow acting coagulant is then added and the whole poured into forms (Figures 198 and 199). The delayed coagulation allows some 10 minutes for the pouring. The coagulated mass is then cured by immersion in hot water for some 20 minutes, removed, whizzed, and dried with gently warmed air. The volume of air in this type of sponge rubber is 4 to 5 times that of the rubber. The upholstering in the new streamlined trains is mostly sponge rubber.

Synthetic Rubber. When crude rubber was bringing $1.00 a pound in 1918, the incentive was strong to develop a synthetic rubber or substitute. To help meet its shortage during the world war, Germany made many tons of synthetic rubbers from polymerized isoprene, CH_2: $CHC(CH_3):CH_2$, and butadiene, $CH_2:CH \cdot CH:CH_2$, prepared from acetylene or benzol. These, however, were poor substitutes for natural rubber, and at lower prices there has been less incentive to improve them. In 1932, however, a new synthetic rubber, Neoprene, was announced, which, while more expensive than natural rubber, has found large uses in gasoline hose and similar products on account of its oil resistance.

This new rubber called Neoprene (formerly Duprene) is made by passing vinylacetylene in gaseous form (50 parts by weight) through a solution of cuprous chloride (25 parts), with ammonium chloride (10 parts), in concentrated hydrochloric acid (175 parts). The reaction vessel is maintained at 30° C. (86° F.). There is formed 2-chloro-1,3 butadiene, also called chloroprene, $CH_2:CCl \cdot CH:CH_2$, with boiling point 59.4° C. (139° F.), at atmospheric pressure, which is swept out at once by an excess of hydrogen chloride. The chloro-butadiene is condensed, mixed with a small amount of pyrogallol and distilled with steam at reduced pressure (100 mm.). The yield is about 65 per cent.

The vinylacetylene is made in a preliminary operation. Acetylene is swept through a concentrated solution of cuprous chloride with ammonium chloride held at room temperature. The issuing gas is cooled to — 70° C. (— 94° F.); the vinylacetylene, $CH : C \cdot CH:CH_2$, with boiling point of 5° C. (41° F.), is condensed, while the excess acetylene is allowed to pass on for re-use. The product is purified by distillation. **The purpose of the rapid sweep through the catalyzing solution is to avoid the formation of undue amount of divinylacetylene. Similarly, in the**

case of chloroprene, the rapid sweep avoids the addition of a second molecule of hydrogen chloride.

The liquid chloroprene polymerizes spontaneously, with no other catalyst than a small amount of air, to a tough and dense jelly, the new rubber. This first polymer, the α-polymer, is plastic; left to itself, it loses its plastic property and becomes elastic in 48 hours at room temperature, or in a few minutes at 130° F. (54° C.), producing the μ-polymer, the cured rubber. Sulfur is not needed. Suitable catalysts are, for the rapid curing with heat, zinc chloride, aniline, naphthylamine, benzidine. If, on the other hand, it is desired to retain the α-polymer, it may be mixed with diphenylguanidine and may then be kept unchanged in the plastic state indefinitely. The stabilizer used commercially is designated as the antioxidant Neozone D.

Artificial latex may be produced in a startling way. The liquid chloroprene is emulsified in water with a small percentage of sodium oleate; the droplets soon polymerize, giving a colloidally dispersed Neoprene. It may be stabilized by adding sulfonated abietene.[8]

The plant in which Neoprene is now (1937) being manufactured has a capacity of 1,000,000 pounds a year.

Reclaimed Rubber. Scrap vulcanized rubber may be reclaimed to yield a product which is an auxiliary to crude rubber in the manufacture of many types of goods. The largest source of scrap is worn-out tires, which are reclaimed chiefly by the alkali process developed by A. H. Marks in 1899. Beads are removed from the tires, and the remaining carcass finely ground and digested in 4 to 8 per cent caustic soda solution at 160 to 200 lbs. pressure for 8 to 24 hours depending on the type of tire, truck tires taking longer. Oils and swelling agents are also added. This digestion removes all free sulfur, destroys the fabric and partially depolymerizes the rubber scrap, which is then washed, dewatered, dried, and "refined" by several passes through a refiner. The latter is similar to a two-roll mill, with rolls only 30 in. long and set very tightly together. The final sheet comes from the refiner .002 to .005 in. thick, and is collected into a slab on a drum. The use of reclaim fluctuates with the price of rubber, annual consumption varying between 20 and 50 per cent of that of crude rubber.

<div align="center">OTHER PATENTS</div>

1,830,749, a compounding process for increasing the resistance of rubber to deterioration due to aging by incorporating a monohydroxy anti-oxidant having the general formula HO—R—R₁, where R and R₁ represent aryl radicals, at least one of which is a phenyl grouping; 1,797,250, process for manufacture of transparent and vulcanized rubber; 1,880,528-9, the reaction product of nitrosanaphthol and mercaptathiazole as an accelerator; 1,832,163, accelerating the vulcanization of rubber by vulcanizing in the presence of carbisopropoxythione disulfide; 1,869,172, compounding rubber, using the still residue from the purification of light oils; 1,862,334, a stock fabricating machine for making pneumatic tires; 1,859,337, a vulcanizing mold for inner tubes; 1,879,194, a vulcanizer for retreading automobile tires; 1,826,091, reclaiming waste rubber; 1,797,243 and 1,806,388, rubber dispersion with potassium oleate; 1,755,891, dispersing coagulated bodies by introducing clay, mixing, and removing the clay by addition of water (W. B. Pratt); dispersing by

[8] U. S. Patent 2,002,622.

means of a solvent, 1,621,468; by means of glue and saponin, 1,732,027; by means of a colloidal substance, 1,731,725; 1,874,546, coagulation of latex emulsion; 1,885,154, process to produce a concentrated and purified rubber latex; 1,850,673, reducing the alkalinity of latex by treating with silica gel; 1,804,157, a creaming agent for latex; 2,029,410, on chemical products and producing same (Neoprene) to Wallace H. Carothers, Arnold M. Collins, James E. Kirby, with 30 examples, 25 claims; 2,002,622, on stabilizing latex.

PROBLEMS

1. In the analysis of a rubber compound, the rubber is first treated with acetone in order to remove or extract the "free" sulfur, and then the sulfur which is "combined" with the rubber, or one of the admixtures, is determined in the residue by combustion for example, or by oxidation, leading in either case to a precipitation in the form of barium sulfate. In a sample under study, the acetone extract is found to give 5.4 per cent free sulfur on the weight of the sample. The extracted sample is shown to have 3.1 per cent sulfur based on the weight of the extracted sample.

(a) What is the percentage of "combined sulfur" in the original sample? (b) What is the percentage of the "combined sulfur" if the original sample contained 5.0 per cent lithopone (29.0 per cent ZnS. 71.0 per cent $BaSO_4$? Note: $BaSO_4$ in the lithopone is filtered off along with any insoluble residue after oxidation, while the ZnS is dissolved.

2. Given the following data on a tread stock, what is the cost per pound, what is the cost per volume, and what is the specific gravity of the resulting stock? What saving is possible if the loading of carbon black can be increased to 28.5 volumes and the present stock is used at a rate of 1,000,000 pounds per month?

	Parts by weight pounds	Cost per pound dollars	Spec. gravity
Smoked sheets	100.0	0.25	.92
Zinc oxide	5.0	.06	5.57
Carbon black	47.0	.06	1.80
Captax	1.0	.50	1.42
Sulfur	3.0	.02	2.05
Stearic acid	4.0	.11	.92
	160.0		

Notes. Make a fourth column with the costs for the weights taken. To find the volume for an item, divide the weight by the specific gravity; call it the pound-volume, and make a fifth column with the pound-volumes. Total it.

The total parts by weight, in pounds, divided by the totaled pound-volume, gives the specific gravity. This should also be the specific gravity of the cured stock (it almost is). Since you are to make a volume loading, you must base it on 100 volumes of rubber, not on weight. For example, the present loading of carbon black is 26.1 ÷ 108.7 = 24.0 volume loading.

To calculate the weight which goes with the new volume loading, remember that this (28.5 volume load) is on the volume of rubber. To place it on 100 pounds of rubber basis, multiply by 1.087. Answer: $2844.

(Cost ÷ pounds) × sp. gr. = cost per "pound-volume," that is, per volume equal to volume of 1 pound of water.

The reason the volume relations are so important is that a given number of molds, with a definite volume, must be filled by the compounded rubber stock which is prepared.

(Much further information will be found in the "Vanderbilt Rubber Handbook, 1936," published by R. T. Vanderbilt Co., 230 Park Avenue, New York, N. Y.).

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A correct appraisal of what advantage may be derived from the patent laws, and a knowledge of its dangers and limitations, are an essential part of the education for the future chemical engineer and industrial chemist.

Chapter 40

Patents*

A patent is a publication, a disclosure, for the benefit of the public, of posterity.

A patent is granted by the government in consideration of the disclosure of a means or method which may be applied to practical use. The purpose for issuing patents is to encourage the development of the practical arts. Inventions disclosed by patents are for the ultimate benefit of the public. As an inducement for creating inventions, and for divulging their secrets, the law offers the inventor a monopoly for a limited period.

This may be a doubtful gift, since the burden of enforcing this monopoly is carried by the patentee, and infringement on the inventor's patent must first be discovered by him, and unless the infringer settles or ceases his infringement, suit must be brought in the Federal courts and prosecuted by the inventor. The law is passive; if the patentee succeeds in proving the charge of infringement, the courts will grant an injunction during the life of the patent and award damages and profits. Frequently it is difficult to prove that there is an infringement, particularly for the chemist patentee, since usually chemical plants are closed to public inspection. However, if there are substantial grounds for believing that there is a case of infringement, the courts will compel the alleged infringer to disclose fully. If the patent is on a chemical product which can be made in only one way, the problem is simpler; but such articles are few. As a rule, the products are well known and can be made in a number of ways, so that the mere selling of the product proves nothing. The infringement of a patented automobile device is comparatively easy to determine, since the invention must appear on the public highways; similarly a new and improved type of cardboard box, suitable for an egg container, necessarily must appear in public, and the question of infringement is comparatively simple to determine. This may not be true with the average chemical patent; the infringer may hide behind factory walls; the article put on sale may reveal nothing as to its method of manufacture. For this reason, not infrequently chemical processes have been kept secret.

Keeping a process secret, however, also involves risk; an unfaithful employee or partner may take out a patent on such process and force the original discoverer to pay tribute on his own discovery. This may seem a harsh rule of law, but the fundamental principle of the patent

* In collaboration with Mr. J. William Ellis, of Buffalo, attorney, and lecturer on patents at the University of Buffalo.

law is that inventive discovery shall be made public for the benefit of the public, and he who chooses to keep the invention secret, must do so at his own risk. A monopoly based on a secret process is unsafe, unless the secret is so thoroughly guarded as to substantially preclude the possibility of outside parties learning the secret.

It goes without saying that no reputable business house will consciously infringe, but will gladly give to inventive ability due recognition and reward. The danger of loss of the monopoly comes from the acts of individuals and corporations in business whose policy is determined by greed rather than principle.

The patent law is rooted in the Federal Constitution and is defined by Congressional statutes.[1] Its purpose is to obtain for the benefit of the public valuable information which will advance the practical sciences and arts, which otherwise might be lost on the death of the inventor. The law is primarily good for the public and, for a limited period, protects the inventor.

Statutory Classes of Invention

The patent statute divides patentable subject matter into four classes: viz., arts, machines, manufactures, and compositions of matter.

1. The word "art" in the statute includes the substantially synonymous terms "process," "mode," and "method." This term includes an act or a series of acts which may be carried out, by hand or otherwise, without reference to any special mechanism, such as the art of dyeing or steel making. The mere function of a machine cannot be patented as an art or process. It is under the heading of an art, method, or process that many chemical patents are granted, although some are granted as compositions of matter.

2. A "machine" is usually a combination of mechanical parts which are adapted to receive, transmit, and modify force or motion to do useful work.

3. The term "manufacture" covers articles or fabric made as finalities and thereby distinguished from machines by not having any rule of action, and from compositions of matter by not involving the relation of ingredients. Examples are a chain, a lamp, or a chimney.

4. A "composition of matter" is a compound of two or more ingredients forming a homogeneous whole, such as paint, glue, ink, or a dye.

Patentability

The subject matter of a patent must involve invention; it must be new; and it must be useful.

(*a*) The question as to whether a creation is an invention is largely a question of fact. No court has been able to give a general positive definition of this term as used in the patent law. Many rules have been made for testing the question of invention, substantially all of which are negative, but they, nevertheless, serve as guides in most cases as well as positive rules. Some of such rules are:

1. Mere mechanical skill is not invention.
2. Excellence of workmanship is not invention.

[1] Article 1, Section 8; the Patent Office was established by Act of Congress in 1790; the first patent was a chemical one, for a process for making potash and pearl ashes (U. S. Patent 1, to Samuel Hopkins, July 31, 1790).

3. Usually the substitution of one material for another is not invention; thus if wood is replaced by aluminum, bakelite, or iron, this does not constitute an invention, unless such substitution produces some new and unexpected results.

4. A change of size is not invention.

5. A change in degree or form is not invention.

6. An aggregation of parts which does not interdependently co-operate to produce a useful result is not an invention; thus the courts have held that a rubber-tipped lead pencil cannot be patented, since the lead and the rubber are not simultaneously used.

7. Mere duplication of parts is not invention.

8. The omission of an element is not invention.

9. The substitution of an equivalent is not invention. The breadth of patent claims depends largely upon the interpretation of equivalents. In general, it may be said that a basic or pioneer invention will have a much greater range of equivalents than an invention making only a small advance in an established art.

10. Using an old thing for a new and analogous purpose is not invention.

(*b*) An invention must be new. This means that the invention must not have been the subject of publication anywhere in the world prior to the date of invention here, and must not have been in use in the United States of America prior to such date of invention. Foreign patents are called publications. Therefore, no valid United States patent can be granted for any invention described in patents issued in countries foreign to this country.

Novelty is not negatived by abandoned experiments; if experiments have been performed and then dropped, even though partially or accidentally performing the function desired, such experiments will not anticipate a later perfected invention. If, however, such experiments are completed and a patent application is filed in the Patent Office within two years after the first public use, a valid patent may be secured.

Prior accidental production is not an anticipation and does not destroy novelty.

The prior use of an invention in countries foreign to this country is not an anticipation; but a prior domestic use is an anticipation.

(*c*) The invention must be useful in the industrial arts. This limitation automatically rules out many freak inventions which would consume the time of the examiners and give nothing of value to the public. An inoperative combination or process, which will not answer the purpose for which it was intended without redesign or alteration, is not an invention.

A scientific principle cannot be patented; a useful application of it to the industrial arts must be presented. Likewise the principle or function of a machine cannot be patented.

Patent Applications. All patent applications must be filed with the Commissioner of Patents at the Patent Office,[2] Washington, D. C. A preamble recites the object of the invention; this is followed by a description of the invention, which must be full, clear, concise, and exact enough to enable any person skilled in the art or science to which it pertains or to which it is connected most closely to make and use the invention. If it is a machine, the description must be exact enough to

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[2] Since 1925, part of the Department of Commerce.

enable its manufacture; if it is a composition of matter, the description must be clear enough to permit the compounding; if the invention is a process, the method of carrying it out must be clearly described.

The claims follow the description and point out the novelty of the invention. For each novel part, a distinct and formal claim is necessary, since patents are not granted except for those novel disclosures which are distinctly claimed. The monopoly granted is limited to the contents of the claims.

The application is accompanied by an oath made by the inventor, setting forth that he is the sole inventor (or if more than one, that they are the sole joint inventors), that he does not know and does not believe that his invention was ever known before his discovery thereof, or patented or described in any printed publication in any country before his discovery thereof, or more than two years prior to his application, or in public use or on sale in the United States for more than two years prior to his application; and further that his invention has not been patented in any country foreign to the United States on an application filed by him or on his authority more than twelve months prior to his application.

Whenever drawings will make the disclosure clearer, they must be presented with the application. In former years, models were required, but they are not any longer.

The fee due on the patent application is $20 when filed, and the final fee for issuing the patent is $20. The fees for design patents vary according to their term.

Patent Office Actions. On receipt at the Patent Office, an application is given a serial number and then goes to one of about fifty different divisions, each one of which handles a single group or a series of related groups of inventions. Each of these divisions is supplied with copies of all domestic and foreign patents and most of the publications on the subjects handled in that division. Each division has one head or principal examiner, and a number of primary or assistant examiners. If the application is rejected because of prior publication or technical defects in the form of the application, a letter of rejection is returned to the applicant or his attorney, setting forth succinctly the reasons for rejection. The applicant or his attorney must secure copies of all references cited by the examiner, and he has one year from the date of the office action in which to amend his application, or point out to the examiner the differences between the disclosures of the publications referred to and his own invention. The wording of his original application may be changed by amendment, but the applicant is not permitted to add any new matter. If the application is twice rejected on the same grounds, such rejection is made final; the applicant may then appeal to the Board of Examiners-in-chief of the Patent Office; from this board, he may appeal to the Commissioner of Patents; from the Commissioner's decision, he may appeal to the Circuit Court of Appeals

of the District of Columbia. The decision of the last-named court controls the action of the Patent Office on the matter at issue.[2a]

Interferences. It sometimes happens that two patent applications for substantially the same invention are pending in the Patent Office at the same time. An interference is a proceeding instituted for the purpose of determining the question of priority of invention between two or more parties claiming substantially the same patentable invention. Patents are granted to the first inventor. The fact that one of the parties to an interference proceeding has already obtained a patent will not prevent an interference, for, although the Commissioner has no power to cancel the patent, he may grant another patent for the same invention to the person who proves to be the prior inventor. The first inventor to file his application in the Patent Office is the senior party to the interference. The burden of proving the date of invention is upon the party who last files his application. If he succeeds in overcoming the date of the filing of the first party's application, then the burden of proving priority of invention shifts to the party first filing. Priority is determined by proof of a series of facts, such as:

(a) the date of the conception of the invention;
(b) the date of the disclosure of the invention to another person;
(c) the date of the first drawings, if any;
(d) the date of the first model, if any;
(e) the date of the first reduction to practice, such as the commercial operation of the invention; the date of filing a patent application is in the patent law a constructive reduction to practice.

The importance of keeping properly dated memorandum books, or notebooks, or other proof concerning the invention will at once be apparent to the young chemist.[3]

If there are no rejections, or if the rejections have been overcome, and if no interferences have been found, the applicant is notified that his patent will be allowed; he is then given an interval of six months within which to pay the final fee for issuing the patent. All patents are issued on Tuesdays. If the final fees are paid on or before a Thursday, the patent will be issued on the fourth Tuesday thereafter.

Searches. Much information as to the advisability of patenting an invention may be obtained by means of preliminary searches. Such

[2a] A bill to establish a Court of Patent Appeals was introduced in the United States senate in January, 1937, by Senator McAdoo. The court would have exclusive appellate jurisdiction to review by appeal final decisions of the district courts; it would have three permanent scientific advisers.

[3] The United States Department of Agriculture had filed suit (in March, 1932), with the United States Court of Customs and Patent Appeals, contesting the validity of U. S. Patents 1,787,416 and 7, granted to Alfred Wohl, of Germany. The patent 1,285,117 issued to Gibbs and Conover in November, 1918, had been cancelled by the Court of Appeals at the time the Wohl patents were issued. The question of the date of "reduction to practice" in the case of each invention became the determining factor The date for Gibbs-Conover is September 7th, 1916; for Wohl, either September 4th or 9th, 1916, depending upon the interpretation of "reduction to practice" by the court. In March, 1934, the court awarded priority to Wohl, and declared the Wohl patents valid. The original application to the German Patent Office by Wohl, of June 28th, 1916, was amended by him on September 4th and again on the 9th, 1916, listing the higher temperature, 350 to 550° C., which had been also stated by Gibbs. The court decided that Wohl was entitled to a date for reduction to practice at least as early as the date of the filing of his amendment. Nothing solid earlier than September 4th could be shown by Gibbs and Conover. This case brings out the importance of the availability of proofs of date and hour of "reduction to practice."

searches may be made for the purpose of determining in advance the patentability or the validity of proposed claims, or whether the invention would infringe prior patents if commercially exploited. These searches are never performed by the Patent Office until after the patent application is filed, but they may be obtained through attorneys who are skilled in this work. In the Patent Office all domestic and foreign patents are classified according to their subject matter. There is no other place where such a classification can be found. It is, therefore, essential that such searches be made in the Patent Office by those who are familiar with the classification.

Patentability searches are made to determine whether an invention is novel and patentable. Such searches are made among the issued patents, and reports upon them are usually accompanied by a few selected copies of the patents closest to the invention searched. Such a search determines the advisability or inadvisibility of filing a patent application. The cost of such searches varies from $5 upward. The search made by the inventor through complete files of patents is usually productive of much waste of time and is inconclusive, since the files of patents in the libraries are not classified and many pertinent patents may be overlooked.

A determination of whether the invention has been in public commercial use is difficult to make. The knowledge of the commercial men of the art is frequently valuable in determining this question, but sometimes a restricted public use may have been made and not be known to those familiar with the general trade. If the invention has been in public use, even though such use is restricted, for more than two years, it will invalidate any patent granted on the invention.

Validity and infringement searches cover substantially all of the patents which come within the scope of the invention in question and are made in order to determine, as positively as can be done, whether the proposed patent, if granted, would be valid, and the invention, if commercially made, would infringe prior patents. Such validity and infringement searches are usually quite expensive and frequently cost several hundreds of dollars. It should be noted that the Patent Office merely determines the question of novelty and does not attempt to determine the question of possible infringements of prior patents; the grant of a patent does not guarantee the inventor that his invention is free from the dominating influence of a prior patent. In expensive commercial operations, therefore, validity and infringing searches are quite important.

Title. The monopoly granted by the patent belongs to the inventor; it is property and the title is vested in him. Such title is absolute and unqualified; the Federal Government can not take it away from him; the State can not interfere. Only a court in bankruptcy can pass title to a patent without the written consent of the patentee; a receiver in a State court may administer a patent but can not transfer the title.

The monopoly granted by the patent is legally transferable. The

patentee himself may pass title to any other person or to a corporation, but he must do so by means of a written assignment. In order that an assignment shall be legally effective against a claim by strangers who did not know of such assignment, it must be recorded in the Patent Office within three months after its date. If such record is not made within the time stated, a subsequent assignee, not knowing of the first assignment, may secure a valid title to the patented invention, if he complies with the law by recording his subsequent assignment, and, in that event, the only remedy of the first assignee is to sue the assignor for fraud.

The patentee, if he pleases, may refrain from making, using, or selling his invention and may decline to permit others to do so. The patentee may retain title to his patent, and grant licenses to operate and sell or use the invention under any desired expressed conditions or within certain territorial limits or for limited periods. The law does not require that licenses be recorded. Such licenses may be either verbal or written. Unless the patentee is a reputable person, the purchaser of the title to the patent may find that previous licenses have substantially detracted from the value of the patent.

Period of the Monopoly. In this country the patented monopoly is seventeen years [4] from the date of the issue of the patent, except that design patents are granted for a period of three and one-half years, or seven years, or fourteen years, as the applicant may elect. Many years ago the law provided that patent monopolies might be extended, but that provision of law has been repealed and now no patent can be extended except by act of Congress. If, however, improvements on the original are made, such improvements may be protected by patent and thereby frequently the monopoly is, in effect, continued for a longer period than the seventeen-year original grant. The original patent may cover the disclosed invention only in a crude way; refinements come with practice, and such refinements may fairly be protected. In many cases the protection on improvements would exist without specific patents on such improvements, since the original invention during the seventeen years' monopoly may so improve the art that successful competition is not to be feared. Of course, such a condition does not apply in all cases.

Disclaimers and Reissues. An inventor may find, after his patent is granted, that he has claimed more than he originally invented or was entitled to. In such case he may prepare and file in the Patent Office a paper containing a disavowal or disclaimer of such excessive claims retaining, however, that part of his invention which is truly his. The patent remains valid for the parts which are justly and truly his invention. Such a paper is called a disclaimer. The advantage of a dis-

[4] In England, 16 years; Canada, 18; Belgium, 20; France and Germany, 15 years. A revision of the French law makes the period 20 years after 1933. In Germany, the period is reckoned from the date of the filing of the application; in this country, it is reckoned from the date of issue, an important difference.

claimer lies in the fact that the danger of invalidity is thus removed if the question becomes an issue in the courts.

A patent may be found to be invalid or inoperative because of inadvertence, oversight, accident, or mistake without fraudulent or deceptive intent; in that case, it may be surrendered to the Commissioner of Patents, who on proper showing will reissue it in the corrected form. The statute does not state how long a period may elapse after the issue of a patent before a reissue must be applied for, but many decisions have held that a lapse of more than two years is fatal to the grant of a valid reissue.

Foreign Statutes. A United States patentee has the right to apply for patents in countries foreign to this country. He must claim these rights within twelve months from the date of filing his application in this country if he wishes to preserve his original filing date; or he may file his foreign patent applications at any time before the actual issue of his patent in this country. If he does neither of these things he loses the opportunity of securing a monopoly in many countries. So far as novelty is concerned, the laws of substantially all foreign countries provide restrictions similar to those existing in this country. Most foreign patents, however, are subject to taxes and in many foreign countries manufacturing of the inventions must be done within a year or more after the grant of the patent in those countries.[5] Unless the foreign taxes are paid and the foreign manufacturing requirements complied with, the patents in most foreign countries are thereby rendered invalid.

No taxes are payable on Canadian patents. In Great Britain taxes are payable only after the expiration of the fourth year of the life of the patent. There are more than one hundred and fifty different countries in which patent laws exist.[6] The question of whether a foreign patent should be taken out depends largely on the subject matter of the invention, and the industrial condition of the country in question.

It should be here noted that an invention patented in a foreign country, and not patented in the United States, may be legally made, used, and sold by any one in this country. Likewise, an invention patented only in the United States may be used by anyone in any country foreign to the United States without violating any legal rights of the patentee.

Infringement. Suits for infringement must be brought in the Federal District Courts by means of a bill of complaint. The defendant files an answer to the bill of complaint. Many defenses may be set up in the charge of infringement such as anticipation by means of prior patents, prior publications, or prior public use, or on the grounds of insufficient disclosure or absence of utility, or inoperativeness, or aggre-

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[5] This is a serious handicap for the American patentee; the foreign patentee who has registered his patent in the U. S. Patent Office is not required to manufacture here.

[6] All countries do not have the same methods or rules for judging and issuing patents. French patents issue immediately and without examination, hence they serve as advance signals for patents filed in other countries, and their factual value is small. German and Dutch patents issue slowly and after painstaking examination, so that they are more apt to be limited to genuinely novel subject matter. The British patents and Canadian patents are about equivalent in stringency of judgment to the United States patents.

gation. Of course, proof of non-infringement is sufficient to cause the bill of complaint to be dismissed.

Prior to the trial of a patent suit in the courts, depositions of fact witnesses may be taken, providing such witnesses live more than one hundred miles from the place of trial. These depositions are taken by either oral or written interrogatories upon examination and cross-examination of the parties to the suit or their attorneys. After being taken, such depositions are filed with the trial court and become a part of the trial record. Experts giving depositions, relating to the subject matter of the patent involved, must give their testimony in open court. The court rules provide that if the court understands the matter and does not desire such experts, such expert testimony is not permitted.

A suit brought for damages, profits, and for an injunction is an action in equity, and is tried before a judge without a jury; a suit to recover damages only, is tried before a judge and a jury.

In former years, probably in 90 per cent of the successful patent suits, claims for profits and damages were waived because of the difficulty of legally establishing them; within the past few years, however, court decisions have modified the rules as to the burden of proof so that it is much easier for the plaintiff to establish proof of profits and damages and much more difficult for the defendant to escape claims for such profits and damages. Recoveries in patent suits are, therefore, much more common now than formerly.

Shop Rights. If an employee in a manufacturing plant makes an invention while in such employ on the time and with the materials of his employer, and thereafter secures a patent on such invention, the company or individual owning the plant has what is known as a shop right or a shop license; that is, the employer can make, use, and sell the patented invention in such plant without the consent of the patentee. The monopoly of the patent, however, outside of the plant, is still solely vested in the patentee. Frequently the employee assigns his patent to his employer and relies on his employer's fairness for his reward. In some companies a contract between the employer and the employee is made, and provides that any invention made by the employee, during the term of his employment, which relates to the business of his employer, shall become the property of the employer. In the case of such contracts, of course, the title to the invention must be legally transferred to the employer. Shop rights, however, under the conditions named, even in the absence of a contract, remain with the employer.

Marking Patented Articles. If patented articles or the containers fail to bear the word "patented," or an abbreviation thereof, together with the date of issue of the patent, no damages or profits can be collected from infringers, unless proof be made that they have had actual notice of the patent. Usually the words "Patent applied for" or "Patent pending" are placed on articles of trade if patent applications have been made, but there is no provision of law requiring such marking, and such marking is regarded only as a warning.

Patent Publications and Services. Annually the Patent Office issues an indexed volume giving the names of all patentees of that year, and a list of the subjects upon which patents have been taken out.

Besides the collection of the full-text patent specifications, there is issued by the various patent offices a journal containing abstracts of the full patents. The United States Patent Office publishes the "Official Gazette of the U. S. Patent Office," in which the abstracts are arranged numerically. For the Canadian specifications, there is published the "Canadian Patent Office Record." The Patent Office in London publishes the "Illustrated Abridgements of Specifications;" since January 1st, 1931, the British Abridgments are classified in 40 groups. A list of these groups with their content in terms of previous classifications of 146 groups, will be found in the Index volumes of the Abridgments, or may be sent for directly. The three publications just mentioned will be found in many of the public libraries in the United States, deposited there free of charge by the several Offices for the convenience of the public. Such libraries will usually have a complete file of the United States full-text patent specifications, also a gift from the Patent Office to the public. Full files of the patents specifications of all countries will be found at the Patent Office in Washington, and may be consulted by any one; given the number, the patent can be found, since they are arranged numerically. On request and payment of a modest fee, a photostat will be sent.

There is one more service offered of the greatest convenience. The Superintendent of Documents, Washington, D. C., will send for $1 the "U. S. Manual of Classification of Patents." After studying it, a request may be addressed to the Commissioner of Patents that all patents in a certain class, or subclass, be sent on, as fast as issued, without further notice; for this service, a fee of $1 per year per class, is charged plus the usual 10 cents for each copy. In this way, the subscriber receives at his desk every patent which pertains to his specialty without any labor on his part.

It will be well to note that the British Patents now have running numbers, beginning with January 1, 1916. Before that time, every year started with number 1, so that for British Patents it was necessary to give the year, as well as the patent number; this is no longer necessary for the patents issued since that date.

Of special value to the chemists' world is the "Chemical Patents Index,"[7] covering the United States patents dealing with chemical and allied topics for the years 1915 to 1924. Two other sources of patents information for United States patents may be mentioned; one is the bi-monthly *Chemical Abstracts* with monthly, yearly, and decennial indexes; the other is the "Annual Survey of American Chemistry."[8]

[7] "Chemical patents index (U. S. 1915-1924)," E. C. Worden, New York, Chemical Catalog Co., Inc., Reinhold Publishing Corp., Vol I, 1927; Vol. II, 1932.

[8] Published (began 1925-26), for the National Research Council, by the Chemical Catalog Co., Inc., or Reinhold Publishing Corp., successors, New York.

Beginning with January 1st, 1928, and with volume 22, the Chemical Abstracts, published by the American Chemical Society, lists patents under the name of the assignee, in addition to the customary listing under the name of the patentee. This is a tremendous advantage for the reader, who often knows which firm is developing a certain patent, without knowing the name of the patentee.

Starting with January 1st, 1935, there is provided as Part IV of the index of the *Chemical Abstracts*, A.C.S., the numbers of the patents, for which abstracts have appeared, arranged in the order of the numbers, and grouped by countries.

British patents will be found abstracted in the *Chemical Abstracts* or in the abstracts of the *Journal of the Chemical Society* (London). A classified collection of German medicinal and dye patents is the *Friedlaender*,[9] while patents dealing with the inorganic chemical industry are classified and reviewed in the Braeuer and d'Ans collection.[10]

Copyrights and Trade-Marks. Copyrights are granted under separate congressional statutes for books, maps, periodicals, drawings, pictures, musical compositions, dramatic works, and the like. Such applications are not made at the Patent Office, but to the Registrar of Copyrights at the Library of Congress, Washington, D. C.

Trade-marks are registered in the Patent Office under the trade-mark laws; labels and prints are registered in the Patent Office under the copyright laws. The Registrar of Copyrights has sole jurisdiction of the registration of everything referred to in the copyright laws, except labels and prints. A label is defined as something applied to the goods or to 'the container; a print is not so applied, but serves separately as advertising. Both labels and prints must be distinctive in appearance, and must be the result of original creation.

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Some important patent decisions are listed in *Ind. Eng. Chem.*, 23, 7 (1931).

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[9] See reading references for Chapter 28.

[10] *Fortschritte der anorganisch-chemischen Industrie*, by Adolf Braeuer and J. d'Ans, in several volumes, published by J. Springer, Berlin.

The German patent law and regulations are stated in the *Chemiker-Kalender for 1932*, Vol. III, p. 574-592, Verlag Julius Springer, Berlin; with a table of sundry patent information covering 23 countries.

"The preparation and prosecution of patent applications," Charles W. Rivise, Charlottesville, Va., The Michie Company, 1933.

"Legal pitfalls for the chemical engineers," J. Davidson Pratt and G. S. W. Marlow, *J. Soc. Chem. Ind.*, **53**, 235 and 261 (1934).

An industrial chemist must have an acquaintance with the appliances suitable for large-scale operations, as distinct from laboratory practice; the proper choice of the specific appliances depends upon such an acquaintance. It would be too much to say that the success of a process depends upon the proper choice of auxiliary devices, but its difficulties will certainly be greatly lessened.

Chapter 41

Appliances Used by the Chemical Engineer
I. Pumps, Fans, Blowers, and Compressors

Pumps are used to move liquids from one point to another, frequently to an elevated point. The simplest pump is the trench pump, which has a short barrel, a piston moved up and down by a hand lever, and, mounted in the piston, a clap valve opening on the down stroke and closing on the up stroke. As the piston is lowered, a gallon or so of water passes through the valve to the barrel above the piston; on the up stroke this amount of water is pushed up and discharged through a lip to a runway.

For industrial purposes, pumps are operated by steam, electric motors, or they may be belt-driven or gear-driven; the latter are known as "power pumps." The variety in principle and design is considerable. A classification might be made as follows:

1. **Reciprocating pumps,** in which the pumping element has a back-and-forth motion, may be further divided into piston pumps, plunger pumps, and diaphragm pumps. The piston pumps are double-acting, that is, each side alternately pushes or sucks; if there is one piston, it is simplex; if there are two pistons, working on the same suction and discharge line, it is duplex; if there are three, it is triplex. The discharge from the duplex pump is more even than that from the simplex. The valves are located in an enlarged portion of the suction and discharge lines.

The plunger pump has a closed cylinder, hollow, as the pumping element. In the vertical type it is single-acting, but usually triplex; in the horizontal type two plungers may be placed, working opposite to each other. The piston pump is usually steam-driven, with the steam piston on the main pump shaft; the vertical triplex plunger pump is usually a power pump.

2. **Rotary pumps** with direct action are those which push the liquid bodily; examples are the gear pump, the sliding vane pump, and the two-vane pump such as the Roots or Connersville. The rotary pumps with indirect action, impelling rather than pushing, hence imparting a velocity, are the centrifugal pumps; the impeller may be "open," or if the vanes are cast between two disks, "closed." A centrifugal pump may work singly, the usual practice in chemical plants, or in stages; each stage has its own impeller and casing.

3. The acid egg, illustrated in Chapter 1, and often called a blow case, is also a pump in the sense that it serves to move liquids, and slurries, from one place to another; the driving force is compressed air, and its operation may be automatic.

A ram is a special type of pump in which the feed water itself supplies the driving force.

Reciprocating Pumps. The structure and operation of the **piston pump** are illustrated in Figure 200. On the stroke from left to right, the water is pushed by the front end of the piston, valves *LP* are depressed, and delivery is made to the pressure line; valves *RS* are held shut by the pressure, so that the suction line is closed. In the meantime and on the same stroke, the crank end of the piston has drawn in water
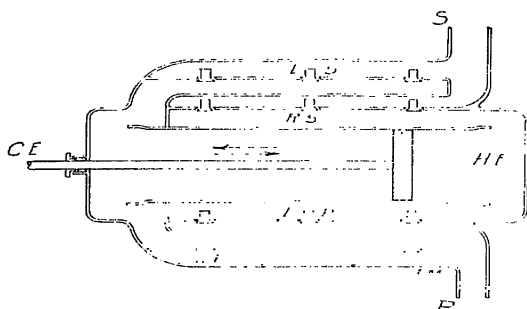
FIGURE 200.—Sketch of a double-acting piston pump. *CE*, crank end; *HE*, head end; *S*, suction line; *P*, pressure or delivery line. *See* text.
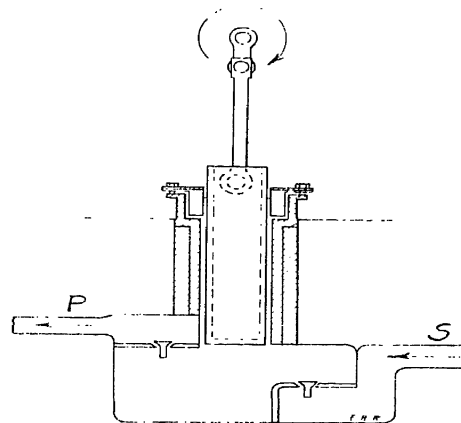
FIGURE 201.—A plunger pump; *S*, suction line; *P*, pressure or delivery line.

through LS, but held RP closed. On the return stroke, right to left, the crank end of the piston exerts pressure, forcing the valves RP open, and delivering the water to the pressure line; the head end of the piston on the same trip draws in water through *RS*, while *LP* stay closed. Such a pump would be double-acting.

The valve may be circular and carry a rubber ring working on a metal seat; or ball valves may be preferred, consisting of a metal ball working against a metal seat, and fitted with shoulders which prevent their unseating more than just enough to let the water through. Ball valves require no spring; they seat by their own weight; but flat valves are held shut by a steel spring, which is chosen so thin that it exerts just enough pressure to seat; the pressure is so weak that very little pressure by the water causes it to unseat. The stem of the valve acts as a guide, causing it to seat properly. In the sketch of the piston pump, the springs holding the valves shut are not shown.

A plunger pump is shown in the adjoined sketch. The plunger is a cylindrical boot, with only one working side, hence single-acting. As shown in Figure 201, the plunger is at the end of the down stroke, and ready to rise. The play of the valves will be clear from their positions.

The piston pump has its packing in the piston itself, while in the plunger pump the packing is in a stationary stuffing box forming part of the casing.

In the boiler house, either piston or plunger pump is used to feed water into the boilers (feed pump); high-speed centrifugal pumps are now also used for that purpose. For forcing a muddy liquid through a filter press, pressures of 40 to 60 pounds are often required and a triplex plunger pump is well adapted. The speed varies greatly with the kind of service performed, but in general, it is rather low, 30 to 60 double strokes per minute.

In the **diaphragm pump** the liquid to be moved does not come in contact with the pumping element. An example of this type of pump is the Dorrco.
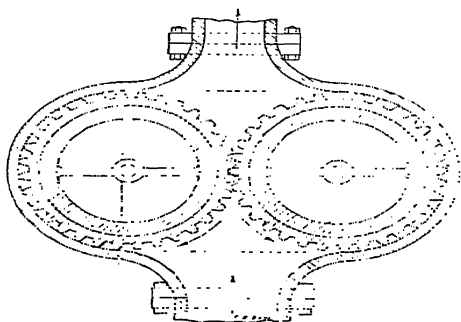
FIGURE 202.—A gear pump.
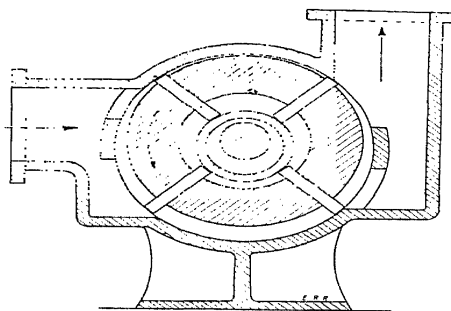
FIGURE 203.—A sliding vane pump, of the ring type.

Rotary Pumps with Direct Action. The gear pump, shown in Figure 202, carries the liquid between the casing and the teeth of the gears. The friction is considerable, and the gear pump is therefore chiefly used for oil and other liquids which have lubricating properties. The size is nearly always small, and the capacity of the pump correspondingly small; its simplicity and reliability have led to its general use for such purposes as pumping fuel oil to the burner.

In the **sliding vane pump,** the rotor and shaft are eccentric to the casing; the rotor carries each slide in and out because they rest on a stationary ring which is centered; the casing itself is circular. This type of sliding vane pump is the ring type[1]; its operation will be clear from the sketch. There are many other modifications of this pump; in the earlier models, the casing was elliptical. The sliding vane pump has again no valve in the strict sense; it has wide passages, so that it is well

[1] Such as manufactured for example by the Taber Pump Co., of Buffalo, N. Y.

adapted for slurries, and for liquids carrying lumps of soft solids. The sizes are rather small; the suction line varies from 1 to 4 inches, although larger sizes may be built and operated with fair efficiency. The pump with 4-inch suction line and 4-inch discharge line has a capacity of 200 gallons per minute at a speed of 150 r.p.m.

In the **two-vane pump,** the action is the same as in the gear pump; the water is pushed between the casing and the vane; the operation is indicated in the four-stage figure adjoined (Fig. 204). Each vane shaft carries a toothed wheel, and the two wheels mesh; one shaft carries the
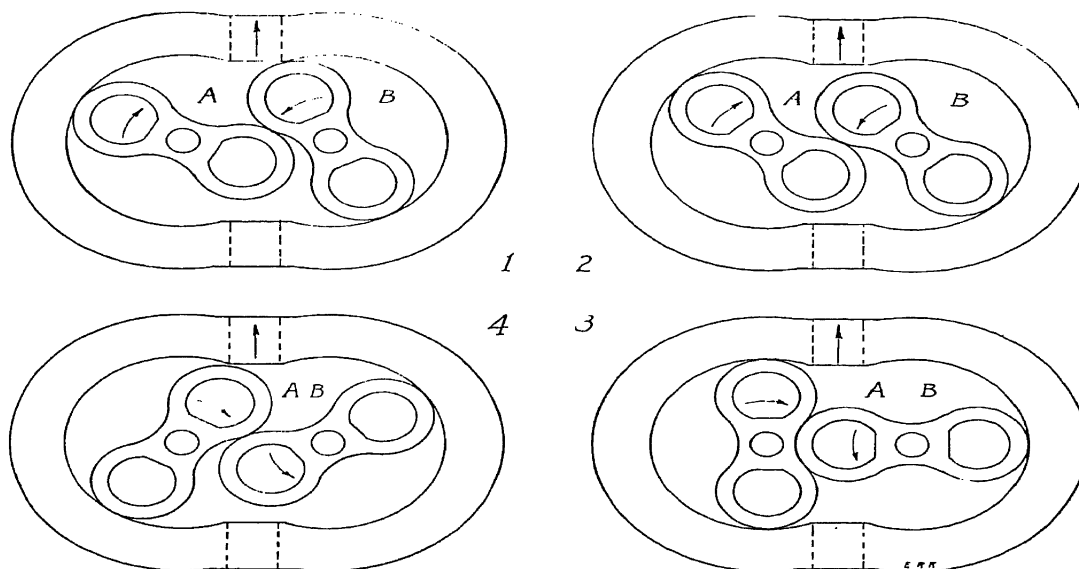
FIGURE 204.—Four stages in one-third of a revolution in a Connersville blower, of the two-impeller type; Stage 1, volume *B* is ready to be discharged; Stage 2, *A* and *B* are a maximum, *B* is beginning to pass to delivery outlet; Stage 3, *A* and *B* smaller than in 2; Stage 4, *A* and *B* a minimum; the difference between *AB* in Stages 1 and 4 has been discharged.

driving pulley, which causes both to rotate against each other. Such pumps are made in small as well as very large sizes; a capacity of 63 cubic feet per revolution is still below the maximum. The speed is moderate (up to 250 r.p.m.).

Centrifugal Pumps. A centrifugal pump is a rotary pump with indirect action. The moving element is a disk, usually vertical, rotated by a horizontal shaft; the disk carries curved blades, and is contained in a spiral casing with close-fitting side walls. The water enters through an opening facing the center of the disk, and the water is caught in the

channels between the blades; the latter do not quite reach the central part of the disk. The water is delivered to the gradually widening spiral part of the casing; it receives from the rapidly rotating wheel a high velocity, and passes out of the casing to the discharge line with essentially the same velocity. Figure 205 is a sketch of a simple, open-impeller type centrifugal pump, single stage. In the two- and more-stage pump, the discharge of the first stage becomes the feed of the second.

Low-pressure single-stage centrifugal pumps are employed with satisfactory efficiency, equal to that of piston pumps, for lifts of 30 to 50 feet (water); the efficiency usually given is 50 to 60 per cent. For lower lifts, the efficiency is higher; for lifts of 90 or 100 feet, the consumption of power becomes enormous and the efficiency correspondingly low. The
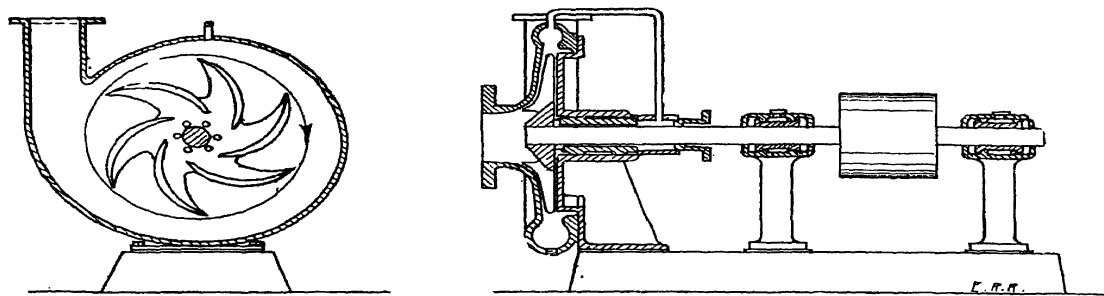
FIGURE 205.—A centrifugal pump, single-stage, open-impeller type.

speed of the centrifugal pump is comparatively high; 1200 r.p.m. is a frequent speed, and 1800 not uncommon. The impeller shaft is directly connected to an electric motor shaft, or belt-driven. The direct-connected pump with its motor forms a compact pumping unit which has come into high favor; it occupies very little floor space, and operates so noiselessly that from a short distance it is impossible to tell whether it is in operation or not. All remarks in this paragraph apply to a single-stage pump; the multiple-stage pump produces higher heads with satisfactory efficiency. For viscous liquids, the centrifugal pump is useless. In giving the heads of the lifts, it is assumed that the level of the water fed in is that of the pump. If the water enters under a head of 15 feet the pump will raise the discharge water that much higher; a slight pressure at the entry to the pump is desirable.

If the water to be pumped must be drawn up from a lower elevation, the centrifugal pump must be primed, that is filled with water, and the whole suction line also, before it can pump. The suction lift must not be over 28 feet, for any type of pump, piston pump included. It may be noted also that the centrifugal pump has no valve, hence is adapted to muddy liquids.

Next in complexity to the open impeller is the closed impeller, usually of bronze, consisting of two disks separated by the curved blades which act on the water; the casing is close-fitting on both sides of the double

disk. The variety in construction is very great. In size centrifugal pumps are built with 20-inch suction line and smaller; in industrial plants, the 3- and 4-inch suction line is the general practice.

For certain purposes, such as fire pumps and boiler-feed pumps, centrifugal pumps are used which are driven at speeds varying between 3000 and 20,000 r.p.m. and even more; for such speeds, it is general to use the steam turbine as the driving mechanism.

The centrifugal pump may be considered a water turbine reversed; instead of a flow of water driving the shaft of the generator, it is the generator shaft which rotates the water wheel and drives the water in the opposite direction (Chapter 12).

Fans, Blowers, Exhausters, and Compressors

For the propulsion of air and gases, fans, blowers, and exhausters are employed. A fan moves a great volume of air (or gas) at slight pressure; for instance it may take the exhaust gases from a blast furnace and deliver them to the base of a tall stack. The word fan covers either blower or exhauster; the blower takes fresh air from the outside and delivers it to a desired point, while the exhauster takes foul air from a certain room and delivers it to the outside air. The essential operation of the blower and exhauster is the same, but the openings in the casings differ.

Fans are volume blowers; compressors are pressure blowers. The compressor delivers a small quantity of air at a high pressure; between the two extremes there are machines which deliver considerable volumes at appreciable pressures, for example 3550 cubic feet per minute at the pressure of 24 inches of water. Such devices are often called pressure blowers, but they may be classified as low pressure compressors. A fan of medium size would be one which delivers 11,400 cubic feet of gas per minute against a pressure of one-fourth inch of water.

A fan may have 6 or 8 flat steel blades, or in a different type, 60 very small curved blades; the latter would belong to the multi-bladed type.

The compressors furnish air or gas at a high pressure, compared to the pressure against which a fan works. The low-pressure compressor described above works against a pressure of less than one pound; it is a single-stage machine, and such single-stage compressors are suitable for pressures up to 50 pounds. For pressures between 50 and 500 pounds, double-stage compressors are used, with an intermediate cooler. For pressures between 500 and 1000 pounds, 3-stage compressors, and for pressures above 1000 pounds, 4-stage compressors are used, with cooling between every two stages. A single-stage compression to a very high pressure is not practical[2]; the heat developed is so great that on cooling in the conduits, a much lower pressure would be obtained. The heat on compressing must therefore be removed, and the cold compressed gas, at 50 pounds for example, may then be compressed a second time.

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[2] The compression curve is too near the adiabatic curve and too far from the isothermal curve.

The fans are generally belt-driven, usually from a special motor. The low-pressure compressor is also belt-driven; the high-pressure compressors are direct-connected to steam pistons.

Multi-bladed Fans. A multi-bladed fan (the Sirocco [3]) is shown in Figure 206. The volume of air moved by the fan depends upon the speed of the wheel and upon the pressure. The higher the pressure against which the fan discharges, the lower the volume discharged; the lower the speed of the wheel, the lower the discharge. Furthermore, the lower the pressure of the air entering the fan, the lower the volume discharged.

The capacity of any fan or compressor is computed on the basis of free air, that is, air at atmospheric pressure and at 60° F. (15° C.); if the gas moved is at an elevated temperature, the volume moved, computed to its true volume at 60° F., will be less than if it had been cold. All these factors are taken into consideration in the tables of capacities which the manufacturers supply on request.
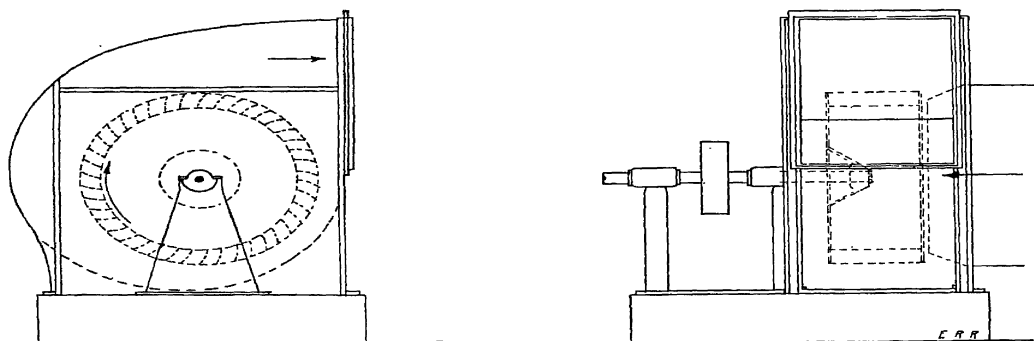
FIGURE 206.—A multi-bladed fan.

Compressors. A low-pressure compressor used extensively in the chemical industries is the Connersville blower, of the same construction as the two-vane pump described in the first part of the chapter. The Connersville blower gives pressures varying from a fraction of a pound to eight pounds per square inch. It is manufactured in all sizes. A medium size would be the 13-foot capacity compressor, which, run at 350 r.p.m., furnishes 4550 cubic feet (calculated) per minute, actually 3640 cubic feet; the difference is due to a slip between the casing and the vane and between the two vanes.

The Nash Hytor is also a low-pressure compressor, furnishing air under pressures of the same range as the Connersville. Its construction and operation will be clear from the sketch (Fig. 207). The eliptical casing contains water which alternately leaves the rotor, and fills it. The air is carried in the buckets formed by the vanes and the liquid,

[3] Made by the American Blower Company, of Detroit, Mich.

from the inlet *A* to the outlet *B*. The small sizes for 50 cubic feet of free air per minute (against 10-pound pressure) have a speed of 1600 r.p.m.; the large size, for 2250 cubic feet discharge against the same pressure, has a speed of 230 r.p.m. The Nash Hytor may be built of special metal, and is used with concentrated sulfuric acid as working fluid for the compression of chlorine gas (Chapter 5).

FIGURE 207.—The Nash Hytor (compressor). *A* and *C* are inlet ports, *B* and *D* outlet ports. The cross-hatched areas represent the gas volume being moved, the clear area within the casing, the liquid employed.
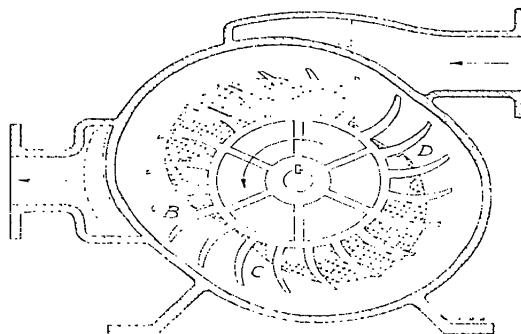
The high-pressure compressors resemble piston pumps, except that the valves are feather valves as a rule. The feather valve (Laidlaw) is a thin flat steel plate, held against the shoulders of a port by a suitable frame. It can lift from the seat one-thirty-second of an inch, or similar distances, which are sufficient to allow the compressed air to pass to the other side of the valve. Cooling between stages is by means of tubes laid in cold water. The development of the direct synthesis of ammonia from atmospheric nitrogen and hydrogen has greatly stimulated the design of high-pressure compression.

VALVES AND PULLEYS

For water lines and for liquids in general, the slot or gate valve is used, especially if the liquid is not under pressure. For steam lines the globe valve is employed; it has a pressure side and a discharge side, and is so placed that the pressure of the steam (also water) is exerted on the under side of the movable disk. In addition to these two, the chemical engineer has utilized the plug valve, operated from a threaded stem above, or from levers with joint below the bottom of a tank. The plug valve has the advantage that on being opened the passages for the liquor or slurry are wide and not easily obstructed. Plug valves are frequently home-made. Besides valves, cocks are used in water and steam lines.

A pump may be driven by a belt which receives its motion from the pulley of a motor; in that case the motor pulley is the driving pulley; the pump pulley, the driven. The number of revolutions per minute of the two pulleys is inversely proportional to their diameters or

their circumferences. For pumps driven by gears the relation of the revolutions per minute is inversely proportional to the relation of the number of teeth on the pinion (small wheel) and gear (large wheel).

OTHER PATENTS

1,849,557, high pressure centrifugal pump of low capacity and economical operation; 1,849,127, a centrifugal pump, especially adapted for pumping more or less viscous materials or fluids such as sewage sludge: 1,863,160, rotary pump consisting of two intermeshing gears; 1,887,873, centrifugal fan, of the propeller type; 1,884,067, a fan for pneumatic blowers; 1,821,484, spiral blade fan, designed especially for use in connection with air-cooled engines; 1,778,041, vertical blower of the propeller type, with a convergent-divergent casing; 1,787,062, multiblade blower; 1,853,973, centrifugal compressor or blower; 1,854,692, compressor and vacuum pump for air and other gases, which has a rotary member which is eccentrically mounted within a cylinder and provided with blades movably mounted in slots and which engage the inner face of the cylinder, thereby forming pockets within which the air is gradually compressed as the rotor turns, due to the progressively decreasing volume of the space between it and the wall of the cylinder; 1,816,403, high-pressure reciprocating piston compressor; 1,867,651, hydroair compressor and vacuum pump (rotary pump having a series of buckets).

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The task of separating a solid from the liquid in which it is suspended presents itself in nearly every chemical plant; this task can be discharged successfully only if the plant chemist is acquainted with all types of devices suitable for such separations.

Chapter 42

Appliances Used by the Chemical Engineer
II. Filters

The separation of comparatively small amounts of solids from larger amounts of liquids is done by settling, followed by decantation of the supernatant clear liquid, or by the use of a filtering device. The separation of very small amounts of liquids from large amounts of solids is done by draining, or by centrifuging.

Settling out the solid is the cheapest method; it is done in many cases; if the operation is extensive, a large capacity in settling tanks is required; these act also as storage tanks. If the liquor is hot, the tank may be insulated by strips of wood. As a rule, this process is too slow; also, the mud collected in the bottom of the tank still contains too much water, and is usually sent through a filter, a combination of settling and filtering.

Filtering devices include the gravity filter, the pressure filters, more commonly called filter presses, and the suction filters. Several points must be considered when studying a filtration problem: whether the cake or the filtrate is the valuable part, whether washing is required or not, and whether the operation should be continuous or intermittent. These considerations will have weight in the choice of the device. Other considerations are capacity, first cost, and operating cost, which includes repair costs and, more important, operating labor. At the end of the chapter, these points will be reviewed.

The suspension to be filtered is called a slurry, if its content in solids is not so high that it does not flow and cannot be pumped; slurries contain from less than 1 per cent to 40 cent of solids, by weight. Suspensions containing more than 40 per cent of solids are more properly called sludges. The solid separated in the filter device is called the cake, the clear liquor running off is the filtrate. The filtering devices such as the filter presses and the suction filters are really frames for the support of the true filtering medium, the filter cloth, which may be cotton duck of various thicknesses, muslin, paper, wool flannel, or metal wire woven into cloth, such as iron wire, nickel wire, and monel wire.

The Gravity Filter. In the gravity filter, the slurry lies over a bed of sand over pebbles, for instance, with channels between the larger pebbles for the escape of the clear liquor. The mud is deposited on the sand; the liquor passes through by the action of gravity. The most extensive use of this type of filter is made in the filtration of drinking water on the large scale (Chapter 13).

A filter paper in a glass or porcelain funnel is a gravity filter; it is used in the fine chemical industry for manufacturing reagents and certain rare chemicals.

The Pressure Filters, Plate-and-Frame Type. The most familiar filter press is the plate-and-frame press; it consists of separate cast-iron square pieces, the plates proper, and the frames, which rest on two horizontal bars, and which may be squeezed together by a movable end-piece working against a fixed front end. The surfaces which touch are machined, so that the fit is perfect. Each frame is covered by a filter cloth which extends over all of it, and on both sides; when the press is closed, the edges of the cloth form the gaskets between the machined surfaces. The cloths are provided with small openings to correspond with the eyes in each plate and frame; in the closed press these eyes form a conduit on one side for the slurry, and on the other side, for the entering wash water. In Figure 208 three pieces are shown: a non-washable plate, a frame,
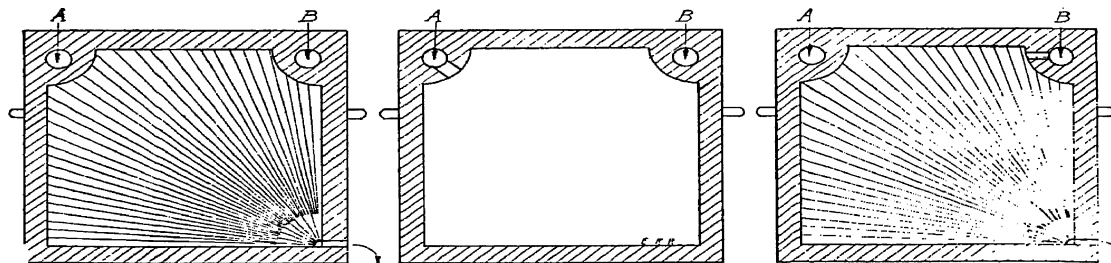
FIGURE 208.—Plates and frame for a filter press; to the left, a non-washable plate; in the center, a frame; to the right, a washable plate; the eyes at *A* form the slurry line, open only to the frame; the eyes at *B* form the wash-water line open only to the washable plate.

and a washable plate. The openings marked *A* form the slurry line; the only port in this line is to the frame. The openings marked *B* form the wash-water inlet line; its only port is to the washable plate, on the right. The non-washable plate has no ports. When filtering, both kinds of plates deliver the clear liquor at the outlet; the slurry enters in the frame, and its liquor passes through the filter cloth in order to reach the channels in the plates. As a rule washing must be done; if the liquid is the valuable part, none must be left in the cake; if the solid is the valuable part, the adhering liquid carries impurities which must be removed. When washing, the outlet of the washable plate, at the left, is closed; the one in the non-washable plate remains open. The wash must now pass through a cloth, through the cake, and through another cloth before it can reach the channels in the non-washable plate and from these, the outlet. The arrangements for filtering and for washing are shown in the two front views of five plates and five frames each.

Slurry is fed to the press until the frame is completely filled with cake; at this point, the pressure in the slurry line increases beyond the usual figure and at the same time, the amount of filtrate decreases. The

washing will be imperfectly done unless every frame is filled with cake. As the first liquor passes through the cloth, it is turbid, and is run to an intermediate receptacle from which it is sent to the filter again; the reason for this turbidity is that the filtering is done not by the cloths themselves, but by a thin layer of mud which coats them in the first few moments. After a few minutes, the filtrate is clear. If the solids are low, it may take 12 hours to fill the frames with mud; two hours is nearer the average time; the difference is due to the percentage of solids in the slurry, and to the size of the frames. When these are filled, the liquor line is closed, and the wash water is admitted through its conduit; the washing may be followed by testing the density of the liquid with

FIGURE 209.—Five plates and five frames when filtering.
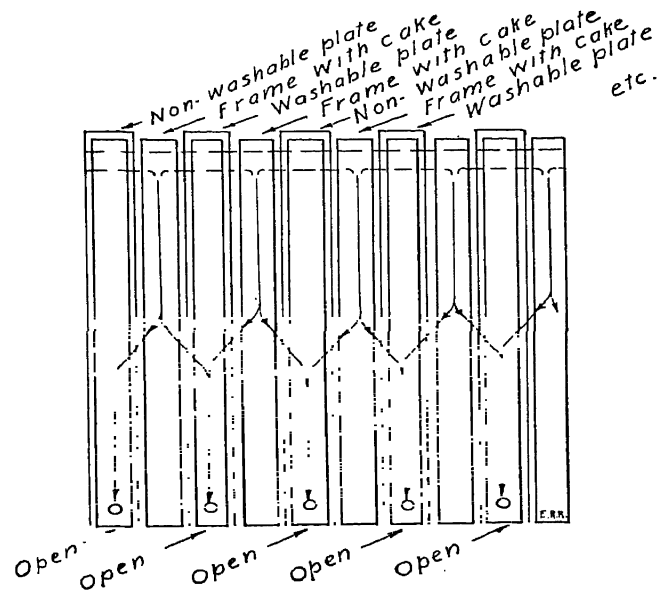
a hydrometer; it is continued as far as the conditions warrant. If the cake is insoluble, and the wash water may be run to the sewer, washing is continued until the water removes nothing more from the cake. If the cake is valueless, only so much wash should be collected as can be reused in the process without concentration, for only when the material is expensive will it bear the cost of fuel for the concentration of weak wash waters. After the washing is carried to the desired point, the press is opened, the plates and frames pushed apart and the cake in the frames dumped into a hopper in the floor, which leads to barrows, or carts, or a screw conveyor. The plates are pushed together again, the press closed, and it is then ready for the next filling.

Instead of a cart, the valueless cake may be flushed away without labor by running the chute into a tank with a stirrer, and feeding a strong flow of water with continuous overflow of muddy water to the sewer.

Good washing of the cake requires that it be not too high in solubles, for as these dissolve, the cake is weakened, it "rots"; as soon as one channel has formed all the water will flow through that, and there will be no washing. For that reason, a different procedure is sometimes used. A first filter-pressing removes the liquor, leaving a "strong" cake, which is not washed in the press. Instead, it is dumped into a tank with stirrer, and there made up with wash water from a later operation; the solubles are now well dissolved, and this slurry is filter-pressed in its turn, and this time it is washed; the "weak" cake is so low in solubles that it will not rot.
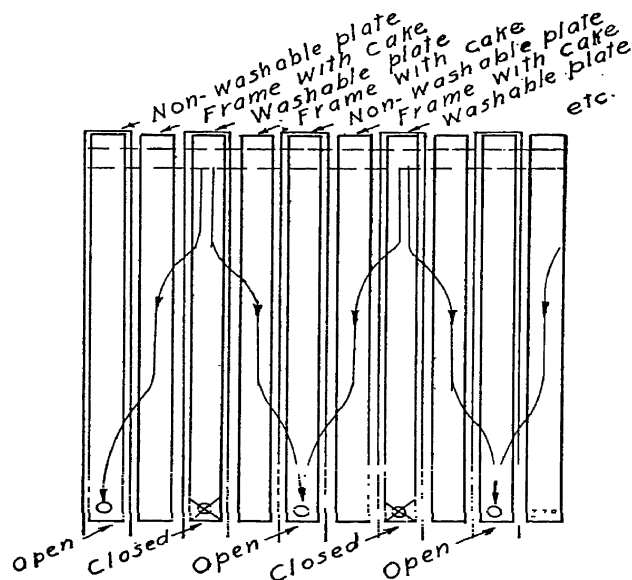
FIGURE 210.—Five plates and five frames when washing.

A press with twelve plates and twelve frames each 12 inches square is a small press; one with 350 circular plates, 5 feet in diameter, is an unusually large one. In ordinary plant work, a press with 49 plates, each 3 feet square, and 50 frames 2 inches thick, is usual; such a press, fed with 20 per cent slurry, whose solids are low in soluble salts, will have a cycle of $2\frac{1}{2}$ hours; three-quarters hour to fill; one-half hour to wash, $1\frac{1}{4}$ hours to dump and close; it will dump 4000 pounds of mud. This figure will vary with the density of the cake, and with other conditions; it is given to indicate the duration and extent of such operations.

Cast-iron is the most common material, but wood is frequently required; other materials rarely. As indicated before, the plates may be circular as well as square. The frames may be thicker, 4 inches for example, so that they will hold more cake; 2-inch thickness is rarely exceeded if washing must be done. The plate and frame may be combined in one, giving the so-called recessed plate; many other modifica-

tions are on the market. Presses are usually opened and closed by hand, by means of a long bar turning the terminal screw which actuates the movable end piece; for very large sizes, mechanical power is used.

The slurry is forced into the pump by means of a duplex pressure piston pump, or a triplex plunger pump, or a blowcase whose principle of operation is similar to that of the acid egg. The pressure varies from 3 to 4 pounds at the start to as high as 40 pounds when the press is full.
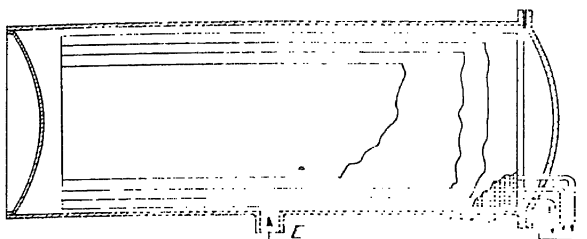
FIGURE 211.—Longitudinal cross-section of a 48 by 120-inch Kelly press, showing filter leaves and slurry inlet at *E*.
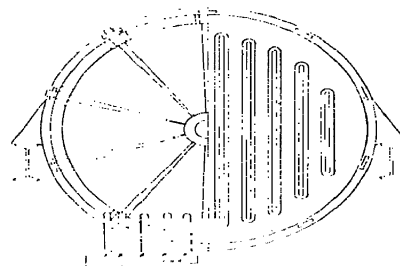
FIGURE 212.—Front view of the Kelly press, with one-half of the movable head plate removed to show the filter leaves.

FIGURE 213. — Cross-section of a filtering leaf in the Kelly press, with cake on both sides, ready to be dumped.

The Shell-and-Leaves Type of Press. In this type of press, light wire frames bearing the filter cloths are provided, which fit in a steel shell; during filtration, the slurry fills the shell, entirely surrounding the cloths; these become coated by the cake, while the clear liquor reaches the inside of the frames and runs off through a pipe connection at the base. In the Kelly press, one of the most successful representatives of this class, the leaves are rectangular, and are fastened to the cast-iron head; the shell is cylindrical, lying on its side. The leaves

and cast-iron head are mounted on a carriage having four small wheels, which run on two rails set inside the shell and on the outside extension of the rails. After the desired thickness of cake has formed, the carriage is pulled out horizontally by chains actuated by a small compressed air motor, and the cake is dumped by jarring the frames with a long pole, aided by a stream of water from a hose. After the cake is dumped, the motor is started in reverse, the carriage is pulled in, and the press closes. The construction is made clearer by the three illustrations adjoined (Fig. 211, 212, 213).

The main advantage of the Kelly press is the ease in dumping; the cake merely hangs onto the frames and is easily dislodged; the amount of hand labor is low. The slurry enters near the center of the shell at its base, from a blowcase located on a lower floor; the filtrate runs out through cocks in the head of the press into a trough which delivers it to a dividing box set at the side, out of the way of the pulled-out carriage. On closing, the chains pull through a toggle joint which forces the head tightly in place and lock it by pushing stout steel bolts into the receiving hoops set in the shell.

If the cake must be washed, the slurry remaining in the shell after complete cake formation is run back into the blowcase, and water introduced. The progress of the washing is followed as it is in the plate and frame press.

Because of the ease of dumping, the cycle for the Kelly is short, and its capacity per day is high. A press 48 inches in diameter and 120 inches long will dump 4000 pounds of washed cake in $1\frac{1}{2}$ hours, distributed as follows: three-fourths hour to build the cake, one-half hour to wash, and one-fourth hour to open, dump, and close the press. These values will vary widely with the percentage solids in the slurry, and with the permeability to water of the cake, and its density. The merits and defects of this press will be discussed after the third type, the automatic continuous suction filter, has been described.

The Sweetland press is another example of the shell-and-leaves type; in the Sweetland, the leaves are stationary, and the shell, which is divided in two halves horizontally, hinged together, opens jaw-like to allow the cake to be dumped.

The Stationary Suction Filter. The simplest type of suction filter consists of a two-compartment box, usually circular; a perforated plate over which the filter cloth is spread separates the two compartments. The slurry is run on top of the cloth; the lower compartment box has two connections, the upper one for a suction pump, the lower one for running off the liquor; the suction pump is connected and the clear liquid passes into the lower compartment. When this is nearly full the suction is disconnected, and the filtrate run off through the lower connection. Usually the size is so proportioned that a batch of slurry may be filtered without interruption. Stationary suction filters of this type are constructed of lead, stoneware, or cast-iron, and have been made as large as 6 feet in diameter. They give good service for slurries with low

percentage of coarse solids, such as a thiosulfate liquor containing some suspended sulfur. The "nutsch" is a similar device, originally rectangular, with the cloth stretched from the sides of the suction box supported

FIGURE 214.—Stationary suction filter or nutsch; *A*, level of the slurry; *B*, filter cloth; *C*, false bottom; *D*, level of the clear filtrate; *E*, suction pump connection; *F*, liquor outlet.
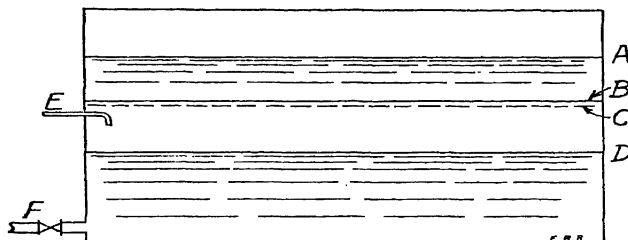
by a false bottom, and accommodating several inches of slurry; gradually the name has been extended to include any stationary suction filter. (*See* Fig. 214.)

The operation is intermittent; the liquor could be removed continuously by drawing it off as fast as it collects, through a separator, to which the suction pump would be connected; the liquor would drop out into the closed separator. But this would not provide for the removal of the cake on the cloth; a shutdown every little while would be necessary in order to remove it. The more solid the slurry contains, the more frequent the interruption. This difficulty is removed in the rotary suction filter.
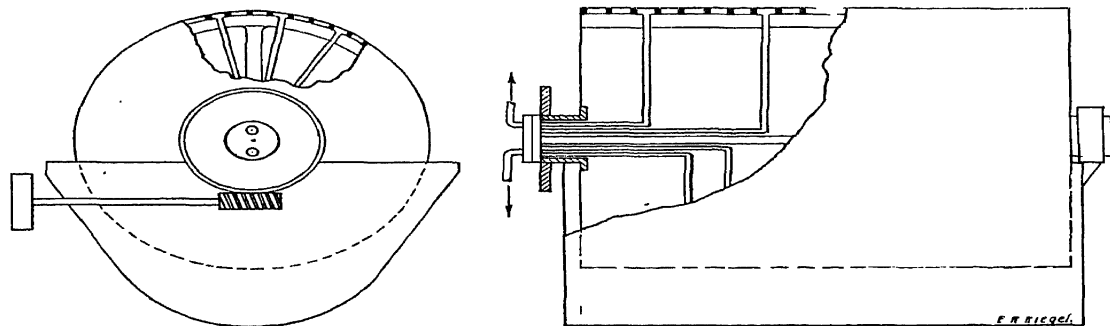
FIGURE 215.—The Oliver continuous suction filter; front and side view.

The Rotary Suction Filter, Drum Type. The rotary suction filter is automatic, and has continuous cake discharge, continuous filtration and wash. One of the well-known examples of this type is the Oliver, which consists of a cylinder or drum lying on its side and carrying the filter cloth, of a knife or scraper for the discharge of the cake, of a tank holding the slurry, and of auxiliary apparatus such as pumps and receivers. The drum is mounted on a horizontal shaft carried by the slurry tank, and dips into the slurry to a depth shown in Figure 216;

liquor is drawn in, and the surface becomes coated with cake; as the drum revolves the cake emerges and meets the wash water which is applied by a spray; as it revolves further, the washed cake meets the discharge knife. At the moment the cloth nears the knife, steam under pressure forces it out slightly, bulging it, causing clear scraping and clearing the meshes. The knife does not bear on the cloth, as that would wear it too fast, but on a wire wound over the cloth, spaced half an inch apart or so.

The simultaneous application of suction for the filtrate, suction for the wash water, and steam (or compressed air) for the blow is achieved by means of an ingenious mechanism, the circular valve. It consists of two halves, one of which rotates with the drum, while the other is held stationary by the liquor lines; a stud set in the rotating half bears on a spring with loose collar which forces the stationary half tightly against the rotating half. The location of the valve is at the end of the shaft as shown in the illustrations. The surface of the drum consists of shallow wooden or cast-iron chambers 12 inches square, covered with sections of one-fourth-inch wire netting to support the cloth. Each chamber has a pipe connection to the valve, running first radially to the shaft, and from there through a main connection which unites the liquor from all sections lying along a horizontal, to a port in the rotating half of the valve. These ports form a circle; the stationary half of the valve has a circular channel fitting over this circle; the channel may be divided into compartments by means of small brass pieces (if the
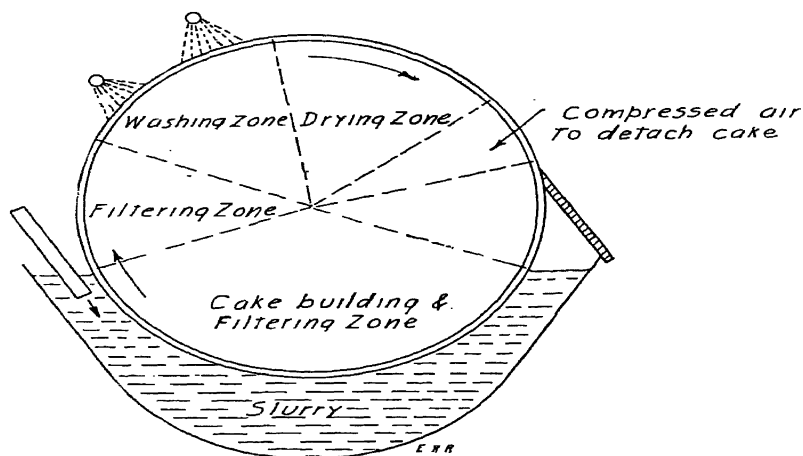
FIGURE 216. — Filtering drum of the Oliver continuous suction filter, showing the filtering, washing, drying, and blowing zones.

valve is brass). One such compartment would form the clear liquor compartment and communicate with the clear liquor line, the next would be the wash-water compartment, feeding the wash-water line; a very small compartment, fitting one port only, would bring the steam blow. Since the bridges are movable, the number of ports in connection with

the clear liquor line may be varied; if increased, for instance, it would have the effect of bringing more drum surface under the action of the clear liquor line; if at the same time the submergence of the drum be increased, which is readily done by raising the level of the slurry in the slurry tank, it will mean a greater zone for cake building. The proper adjustment of the stationary half of the valve is made through a special valve rod.

FIGURE 217.—Assembly for a small-scale Oliver suction filter; 1, filtering drum; 2, filter valve; 3, discharge knife; 4, slurry tank; 5, separator for filtrate; 6, liquor pump for filtrate; 7, separator for wash; 8, liquor pump for wash; 9, to the suction pump; 10, valve for reducing the suction on the wash area.
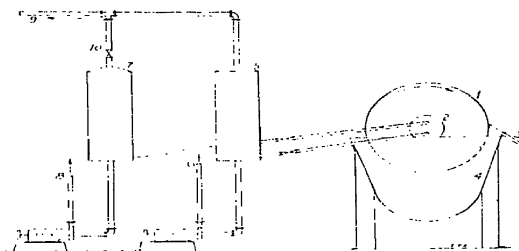
The valve surfaces are machine-faced to give perfect surfaces; they are lubricated from two or more pressure grease cups; the wear is slight because the drum revolves once in 7 minutes, or similar speeds. Each port fits perfectly against the inset bridges, so that no internal leaks can take place. For alkaline liquors, the valve should be of cast-iron.

A suction pump pulls out the liquor and any false air which has leaked in, to a separator, wherein the liquor drops to the bottom and is pulled out by a separate liquor pump, while the air rises and is removed by the suction pump. The same suction pump serves for the wash water, but the suction is reduced by means of a reducing valve, for it is well that the filtrate be pulled in rapidly, but a definite period of time should be provided during which the wash water may remain in contact with the cake. The wash is pulled through a separator, from which the wash liquor is pulled out by means of a separate pump. A complete assembly is shown in Figure 217.

The cake is discharged by the knife onto an apron, and from there may be removed by a screw conveyor. The feed of the slurry to the tank, the drawing off of the clear filtrate, the application and removal of the wash water, and the discharge of the cake are simultaneous and continuous functions; if the cake is removed automatically, the filter is automatic; no labor of any kind is required. It has considerable flexibility, so that it may be adapted to a great variation of slurries. If the percentage of solids is high, the drum revolves fast; if the percentage is low, the drum is made to revolve slowly; if no washing is needed, the submergence may be great; if washing is important, the wash zone is extended. The filter cloth is chosen from the wide choice of material for maximum service. It is no wonder that the automatic continuous suction filter has been very successful.

Its main limitation is that of pressure, since the atmospheric pressure,

14.7 pounds, is the maximum, and all of it is rarely applied. With volatile solvents which must be filtered hot, this type of filter fails, for the solvents volatilize, and no liquid at all, in the worst cases, can be pulled through the cloth. With concentrated, warm salt solution in water, the filter functions well, if the temperature is not over 70° or 75° C.

Dorrco Filter. In the Dorrco filter, which is also a rotary suction filter with continuous operation, the sludge is contained within the drum, whose inner wall bears the filtering medium. The dewatered, washed cake is discharged into an inner trough. There is greater case in filtration, in that the coarser particles settle out against the filtering cloth, with the finer ones drawn in only later; the plugging of the filtering cloth should be less likely. Another advantage in this novel design is that the drum can run on idling rolls.

Rotary Suction Filter, Disk Type. The American Continuous Vacuum Filter represents the disk type among the rotary suction filters. It is a well-known filter which has been established in plant practice
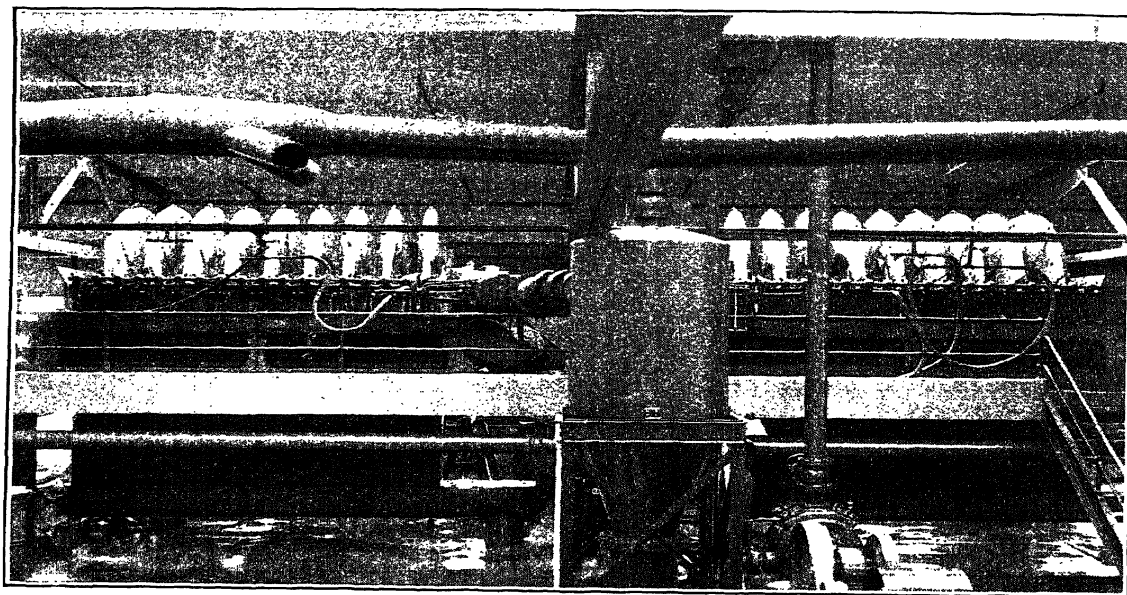
FIGURE 218.—Twin unit of an American Continuous Disk Suction Filter, showing two 9-disk units, separator and pump, as well as conveyor box on the floor for the filter cake. (Courtesy of the Oliver United Filters Corp., Hazleton, Pa.)

for many years. The filtering medium covers flat disks which are mounted centrally on a hollow shaft through which suction is applied to the under side of the filter cloth. The assembled shaft and disks are in turn mounted upon the slurry tank. The disks revolve with their lower portion in the slurry; as they emerge, the cake dries and wash

may be applied. At the discharge point, just before entering the slurry again, small rollers remove the cake which can drop downward because at that place the slurry tank is deeply notched. The suction pipes from the various disks terminate in the rotating part of the valve, while the stationary part carries the liquor and wash lines. The valve is faced
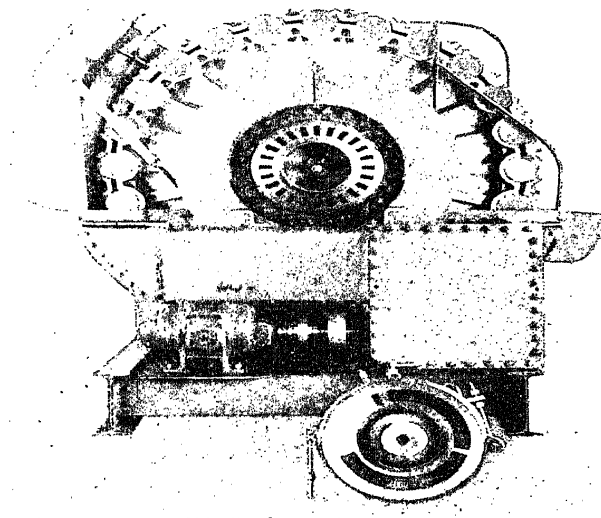
FIGURE 219.—End view of a 24-tube unit of the oscillating continuous filter, Genter type, with valve plug exposed. The tubes extend horizontally, away from the reader. Note the 24 ports in the rotating half of the valve, and the 3 ports in the stationary half, on the floor. (Courtesy of the Bartlett Hayward Company, Baltimore, Md.)

and not flat, but of the conical plug type which possesses the important advantage of seating itself as a slight wear takes place. This filter requires auxiliary devices such as the drum type suction filter does, separators, suction pump and liquor pump.

Multitube Rotating Suction Filter. The oscillating continuous suction filter * (Genter type) consists of a number of slender tubes arranged in a circle on a disk which oscillates as well as rotates. The tubes form a sort of squirrel cage; they are under suction while submerged in the slurry, and when receiving a wash spray. Each tube is connected to one port of the rotating half of the valve, whose stationary half has a port for filtrate, another for wash-water, a third, small one, for the air blow. The cake is wiped off by two wipers or scrapers, one above, the other below the tubes. (*See* Fig. 219.)

The Continuous Pressure Filter. The limitation of pressure has

* The Bartlett Hayward Company, Baltimore, Md.

been removed by the development of the continuous pressure filter, which resembles the suction filter, but has a casing over the drum in addition, so that pressure above atmospheric may be applied; also a closed box for the screw conveyor and a receiver for the cake must be provided. The suction filter will continue to be used whenever possible, since it is simpler; in special cases the pressure filter will have to be substituted.

Comparison of the Several Filters. On closer study, it will be found that every filter has its field which it serves better than any other; the various types supplement each other. The plate-and-frame press is the proper device for a process requiring one dumping a day or in several days, for then the press may be put together with care; the surfaces cleaned to give tight joints. For a cake which is valuable, so that the dumping is a cautious operation, there may be several openings per day and yet this press may be the best choice. But for a valueless cake, in a press worked to capacity, opened five or more times per nine-hour day, it will be closed carelessly, especially if it is of large size. To bring the plate together, 100 plates or frames may have to be pushed along the two horizontal bars; unless these are clean and well oiled, the press will not be tightly closed. Unless the frames and plates are absolutely free from grit, the surfaces will not meet and there will be a leak; even if the leaking liquor is recovered, and sent back to the press, it is a waste of filtering capacity. Every joint between plate and frame is a potential leak, hence in a 50-frame press there are 100 such possible leaks. In this respect the Kelly press is greatly superior; it has one gasket, hence only one possible leak; to keep one gasket clean is a reasonable task, and as a result, it rarely leaks. The Oliver has no possibility for leaking except in the valve, and that is easily refaced.

The plate-and-frame press has a valuable feature in that the filtrate is visible; should one plate run dirty, it may be shut off and the filtration continued with the remaining plates; the Kelly press has the same valuable feature; in the Oliver, it is missing; if there is a break in the cloth so that mud enters, there is no way of detecting the faulty place, and all the filtrate is slightly muddy. The blow of steam or compressed air cleans the cloth too well, in some cases, so that the fine layer of mud must reform, and while it does, the liquor runs slightly muddy; this constitutes a fault in the Oliver which is absent in the other two filters; if a slight turbidity does not matter, the great economy of the Oliver and similar suction filters will place it first; but if absolute clarity is required, the older presses are superior.

Both Kelly and plate-and-frame presses suffer from the fact that their operation is discontinuous; in that respect the automatic suction filter and the automatic continuous pressure filter are supreme.

Strictly speaking, filtering and washing mean a separation of the insolubles from the liquor, followed by a displacement by water of the liquor adhering to the solid. A good example is the ferric hydrate and lime mud in the solution of sodium sulfate. More than that should not

be required from the filter. Frequently salts present in the solid state must be dissolved during the "washing"; this leads to rotting of the cake. This will have serious results especially in the Kelly press, because there the cake is unsupported, and if the structure is weakened by removing salts, the cake drops off in the shell, clogging the inlet and otherwise interfering with smooth operation. Another slight drawback to the shell-and-leaves type press is the necessity of running back to the blowcase a shellful of slurry once the cake has reached the proper thickness, before the press can be opened.

The centrifugal basket is also a filtering device, and very successful; because it is primarily a means of rapidly draining a wet solid, it is described under that head in Chapter 43.

In first cost, the plate-and-frame press is the lowest; its operating cost is the highest, but if the slurry is low in solids, requiring infrequent openings, it remains the most economical device. For the rapid handling of cake rich in solubles which need not be washed in the press, because the mud after dumping is reslurried, the Kelly or Sweetland will give excellent service. For a mud which must be washed with so much liquor that continuous operation is desirable, the rotary automatic suction filter, either of the drum type, like the Oliver, or the disk type, like the American Continuous Filter, is indicated.

OTHER PATENTS

U. S. Patent 1,870,485, multiplex rotary drum filter; 1,859,282, continuous filtering apparatus for removing clay, fuller's earth or other fine material, from oil; 1,799,768, dual fluid filter using two filter media; 1,812,773, a filter for filtering suspended solids from liquids, consisting of a vertical, tapered tube filter press.

PROBLEMS

1. A Kelly press dumps 4000 pounds of cake once in $2\frac{1}{2}$ hours, with one man operating the press. A plate-and-frame press dumps 4000 pounds in $2\frac{1}{2}$ hours, requiring two operators. What is the figure for hours of labor on the basis of one individual (called man-hours) per 1000 pounds of cake? Inspection and repair labor is left out of consideration. If the Oliver is completely automatic, what will its man-hour figure be? Make a table comparing the three values.

2. An Oliver filter drum 4 feet in diameter and 6 feet on the face makes 1 revolution in 6 minutes. What is the circumferential speed? In order to raise the circumferential speed by one-half, how much faster must the filter revolve? How many square feet of surface has the drum?

3. Thirty-two thousand pounds of wet cake are dumped per 10-hour day from 8 plate-and-frame presses. If each frame holds 80 pounds of wet cake, how many frames has each press?

4. A slurry carries 10 per cent of insoluble mud, on the dry basis, that is, determined dry. How many pounds of liquor form while 10,000 pounds of cake are collected in the presses? If the density of the filtrate is 1.44, how many cubic feet of liquor are collected? If the density was 1, it would take 62.5 pounds for 1 cubic foot. How high would the filtrate liquor stand in a circular tank 12 feet in diameter? It is assumed that all the liquor is forced out of the cake and collected; this is very nearly, but not quite, realized by blowing the cake with steam.

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In the course of the growth of the chemical industries, a number of appliances have been devised which are characteristic of these industries. Their application has become great enough so that engineering firms devote themselves not only to a single type, such as evaporators, but to the best design of the evaporators for specific industries, for example, evaporators for beet-sugar liquors, or milk, or glucose concentration.

Chapter 43

Appliances Used by the Chemical Engineer
III. Evaporators, Driers, Cottrell Precipitator, and Others

Among the appliances which have been perfected to a high degree of efficiency are the evaporators, whose heat source is usually steam; the most economical form, the triple-effect evaporator, reduces the fuel consumption to almost a third. The concentration of a dissolved salt yields a liquor which on cooling deposits crystals; these are separated from adhering mother liquor on a drain board, or more rapidly in a centrifuge. In many cases the substance must be absolutely dry, and this may be done in cabinet driers, vacuum driers, or most economically, in a rotary drier. Crystallizers and driers are important appliances.

An appliance not far removed in form and in principle from the type of drier known as the drum drier is the chip machine, which permits the rapid production of many substances in the form of thin chips which possess properties making them much superior to lumps.

The dust collector, the Dorr thickener, and mixers for pasty solids are frequently indispensable.

An electrical appliance which the chemical engineer uses freely is the Cottrell precipitator for dust and mists.

Evaporators. The simplest kind of evaporator is the open kettle hung over a fire, or the open pan, in the path of waste heat gases. Heating by means of steam, either in coils or in a chest with numerous horizontal (or vertical) tubes placed in the liquor is the usual practice; the vessel is closed, except for an outlet for the steam rising from the liquor, and this outlet may be closed by a valve. The use of steam in the coils permits a closer regulation of temperature, and the closed vessel allows the transfer of the contents to an elevated point by applying compressed air, on the principle of an acid egg. The single evaporator, working at atmospheric pressure, is largely used for the concentration of a solution which remains clear while in the evaporator, and deposits crystals only as it cools after transfer to the crystallizers; for such cases, the steam chest may be placed near the bottom. In the case of sodium chloride, there is a separation of the solid as the evaporation progresses, and it accumulates at the base of the vessel, in the conical part provided; the salt in the cone is more or less undisturbed, because the steam chest is

situated well above it. For such a case as glycerin from a soap kettle, the concentration is performed at reduced pressure; the salt is removed at intervals without interrupting the evaporation, by the aid of a salt box which is also under suction; by closing the valve at the base of the cone, the salt box can be emptied, then closed again, and evacuated, when it is ready to receive another salt dump.
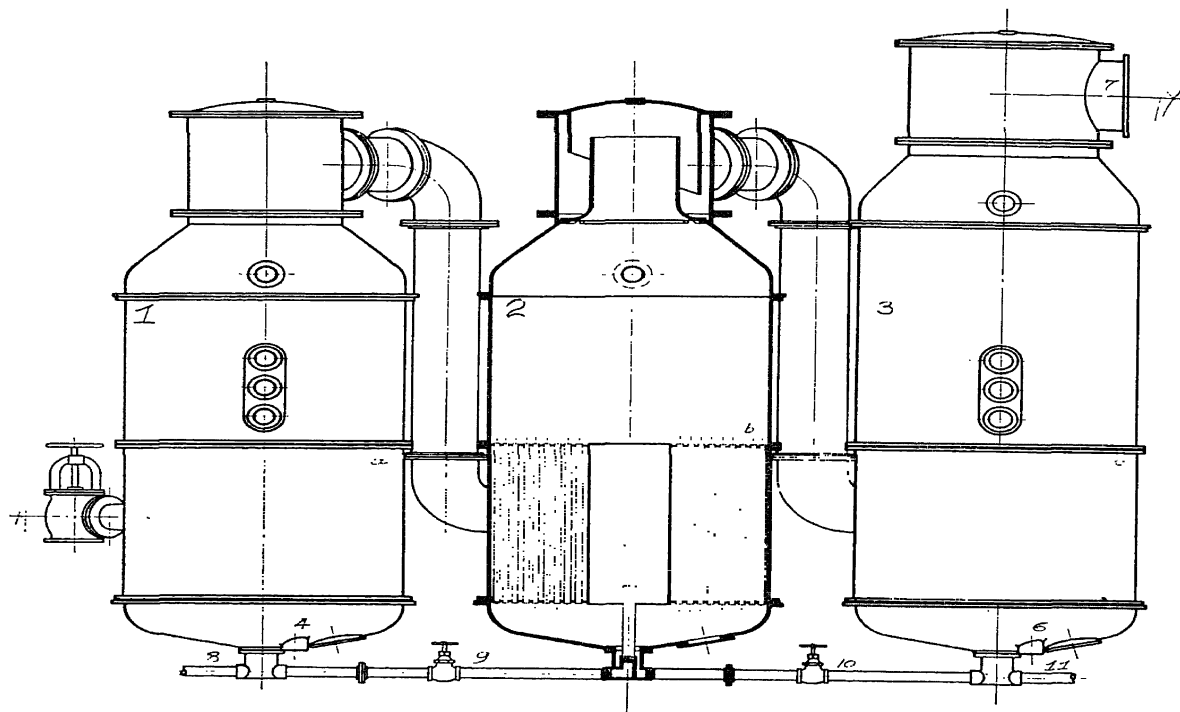
FIGURE 220.—Sketch of a triple-effect evaporator. Boiler steam enters steam chest a, with outlet 4 for condensed water; the steam from solution in No. 1 enters steam chest b; the steam from No. 2 enters steam chest c with outlet 6; the steam from No. 3 goes via 7 to condenser. The reduced pressures are given in the text. The weak solution enters No. 1 at 8; after concentration, it passes from No. 1 to No. 2 through 9, and after further concentration from No. 2 to No. 3 through 10. The concentrated liquor leaves No. 3 through 11, periodically. (Courtesy of the Geo. L. Squier Manufacturing Co., Buffalo, N. Y.)

For a number of products, the fuel item is so important that the triple-effect evaporator is used; familiar cases are the salt (NaCl) and the sugar industries, particularly beet sugar. The triple-effect evaporator depends upon the fact that the boiling point of any liquid in a closed vessel from which the atmospheric air has been removed is lower than in the atmosphere, and furthermore, the lowering in the boiling point is roughly proportional (not absolutely) to the lowering of the pressure. The normal atmospheric pressure at sea level is **29.92** inches

of mercury; the vacuum in the various vessels is expressed in inches of mercury which are forced upward by the air pressure against the pressure in the evaporator; an absolute vacuum is shown by a column 29.92 inches high, since then the pressure inside the vessel is nil.

The connection between the several effects is shown in Figure 220; the vapor from the central plant enters the first steam chest and causes the liquor to boil. The steam from this liquor passes to the steam chest of the second vessel, where it becomes the source of heat; after giving up its heat to the colder liquid it is liquid water, which is trapped off at the outlet from the chest. The steam arising from the liquor in the second vessel becomes the heating steam in the third chest; the water vapor rising in this third vessel passes to a condenser, where cold water returns it to the liquid state. An example from the concentration of sugar solution follows [1]:

	Vessel 1	Vessel 2	Vessel 3
Vacuum	2½ inches	14½ inches	26 inches
Temperature of entering steam....	220° F.	→ 205° F.	→ 183° F.
Temperature of boiling liquor......	205 —	183 —	130 → condenser
Temperature fall in each vessel....	15	22	53

The same quantity of heat raises steam three times, and the saving in fuel is almost two-thirds; there is a consumption of steam running the suction pump; theoretically, it is only such as is required to pump out the vessel to the required pressure; practically, the pumping must be continued throughout the evaporation, because some air leaks in, and the liquor gives up dissolved gases, but even so, the steam consumed for the pump operation is very small, and the fuel consumption is cut nearly to one-third. There is an additional advantage in that boiling at low temperature gives a better product. Double effects and quadruple ones are also used [2]; more than four are not practical.

For such an inexpensive product as salt (NaCl), the saving in fuel is most important, and triple and quadruple effects are commonly used in salt plants. They are of special construction, with conical bottom ending in a rising boot which permits constant discharge; in point of size, the evaporators for salt are probably the largest, as large as 30 feet diameter. The 20-foot diameter pan is quite common, with an over-all height of 50 feet. The material is usually steel, but at least one triple effect for salt is of copper lined with tin.[3]

For sugar solutions, the liquor in the first pan is pumped to the second pan, there to be evaporated further; while in turn, the liquor from the second pan is pumped to the third pan, for still further concentration. In the salt plants, each effect receives brine of the same strength; the fuel saving is realized in either case.

Not only solutions of solids, but of high-boiling liquids are concen-

[1] "The manufacture of sugar from the cane and the beet," T. H. P. Heriot, New York, Longmans, Green & Co., 1920, p. 259.

[2] An example of quadruple-effect operation will be found in *Ind. Eng. Chem.*, 10, 195 (1918).

[3] *Bur. Mines Bull.* No. 146, W. C. Phalen, contains numerous illustrations of multiple-effect evaporators for salt (1920).

trated in single- or multiple-effect evaporators. A single vessel operating under greatly reduced pressure, and receiving, usually, highly concentrated solution from preceding evaporators, is called a vacuum pan.

The important study of fractionating columns for the separation of liquids by taking advantage of the differences in their vapor pressure has been touched upon in Chapters 20 and 24. In the reading references, there will be found grouped together valuable articles, which will afford the beginning of a scientific study of fractionating columns.

Crystallizers, Drain Boards, Centrifugals. The liquor from the evaporator, after suitable concentration, is blown, or pumped, to shallow vessels, of steel if possible, or wood or lead-lined wood, if necessary, where it deposits crystals on cooling. As a rule, the liquors are at rest;
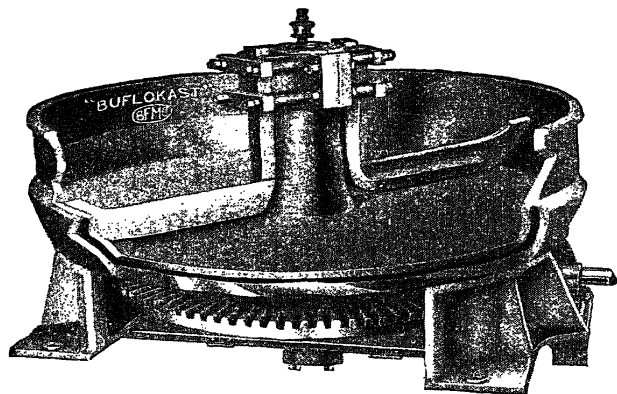
Figure 221.—Jacketed crystallizer with rotating arm, for the production of small crystals. (Courtesy of Buffalo Foundry & Machine Co., Buffalo, N.Y.)

for the production of small crystals, a circular pan with slow agitation by a rotating arm is used, and by jacketing the pan, the temperature may be controlled. After crystallization the mother liquor is run off, and the wet crystals may be piled on a drain board which slopes toward the crystallizer; a more rapid way of removing adhering liquor is by dumping the crystals into centrifugals, and after the proper charge has been added, setting the basket in motion; the mother liquor is whirled off and is caught in a circular apron. The modern centrifugal is driven from overhead, by direct-connected motor, and has an annular ring in the base which can be lifted for discharge through the bottom. A conveyor belt travels underneath and conveys the crystals to the screen, or drier.

Driers. Moist solids may be dried on trays placed in a closet, with a few steam coils at the base. A cabinet drier is a closet with trays, fitted with a motor-driven fan and suitable partitions so that the air is circulated; steam coils raise the temperature of the air to the desired point. Vacuum driers are tray driers [3a] in strong iron boxes which may be evacuated; the trays stand on shelves which are hollow, and in which

[3a] *See* Fig. 165.

heated water, steam at various pressures, or oil heated still higher, may be circulated, so that a wide range of temperature is possible.[4] The rotary drier is gaining on all other forms, however, because of its labor-saving feature, except for small-scale operation, and for special cases. The rotary drier is a long cylinder lying on its side, resembling the Portland cement furnace, but of light construction; warmed air is pulled through the cylinder, which travels in a direction opposite to that of the solid. The latter is fed in at one end, and moves to the opposite end gradually, by virtue of a slight inclination. A tunnel drier consists of
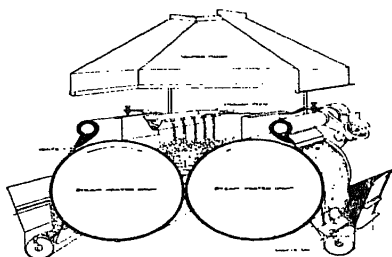
FIGURE 222.—Atmospheric double drum drier, with liquid feed. The slowly revolving hollow drums are steam heated. The dry coat is scraped off as shown; each collecting box has a screw conveyor. (Courtesy of the Buffalo Foundry & Machine Co., Buffalo, N. Y.)
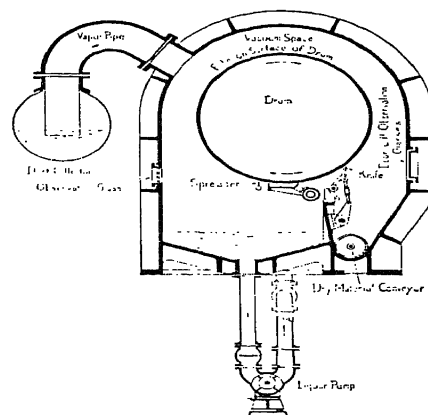
FIGURE 223.—Cross-section through a vacuum drum drier. The suction is applied to the dust collector, just behind the vapor line. The 2 boxes for the dried material not shown. The slurry is pumped to the small trough next to the spreader, and constantly overflows. (By courtesy of the Buffalo Foundry & Machine Co., Buffalo, N. Y.)

a long chamber through which small cars carrying the material are slowly or periodically moved one way while warm air travels the other way. The atmospheric drum drier consists of two hollow drums rotating toward each other, and internally heated by steam; buttermilk or tanning extract, for example, lies between the two drums; a thin film is carried down by each cylinder, and dries in a fraction of a revolution; a scraper detaches the powder. The speed is slow. The drums are furnished chromium plated, if desired; the evaporator may then be used for a number of products which would attack iron. The same evaporation may be performed at reduced pressure by placing the drum in a

[4] The shelf drier may be used at atmospheric pressure, and it may be circular and provided with rotating arms; for several shelves, the material may be moved from one shelf to another alternately, with central, then circumferential discharge; *compare* Chapter 4 under anhydrous bisulfite of soda.

housing, providing a suction pump, a small condenser, and a conveyor with store boxes inside the evacuated area; such vacuum drum evaporators are suitable for drying dyes and for milk evaporation (copperlined).

In the Flick catchall and entrainment separator, the vapors enter tangentially, so that a circular motion is set up. (*See* Fig. 225.) The droplets or other suspended particles are thrown to the inner wall, and pass through its slits to the chamber between inner and outer wall, out
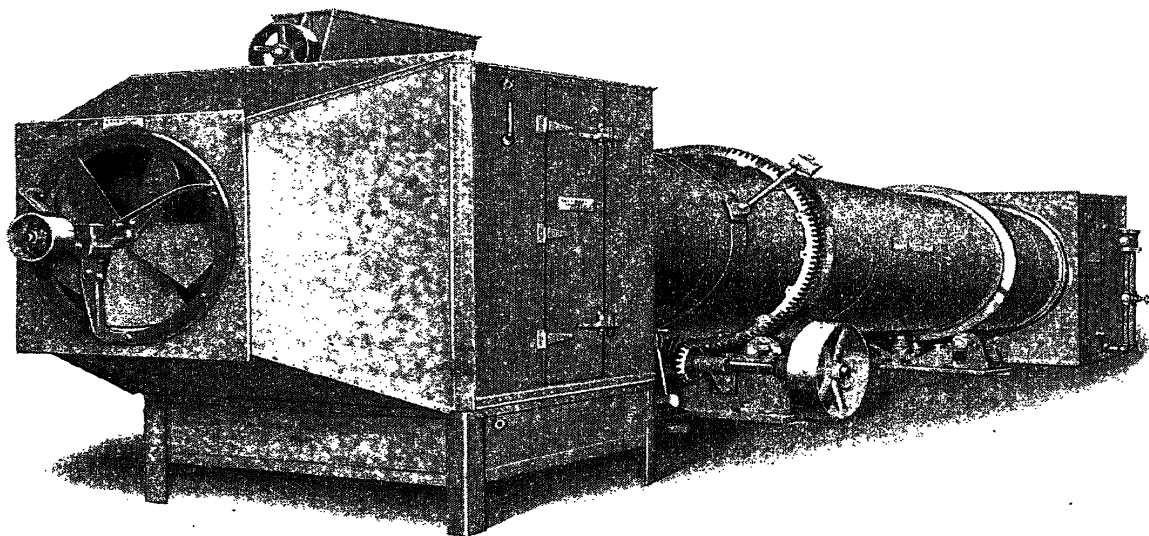
Figure 224.—A rotary drier, from the exhaust chamber end. The fan draws air, warmed over the heating coils at the other end, through the cylinder which slowly rotates. Longitudinal ribs lift the material and dump it when they reach the highest point in the rotation. The feed is at the suction end. (Courtesy of Geo. L. Squier Manufacturing Co., Buffalo, N. Y.)

of the path of the vapors or gas. The droplets collect and drain to a bottom discharge. The cleaned vapor leaves at the top of the separator. Such a separator is used between a single or multiple effect glycerin evaporator, for example, and the vacuum pump or ejector; any entrained liquid is recovered.

Dust Collectors. The gases from a blast furnace carry with them solid particles in the form of dust; the greater part of this dust may be recovered by passing the gases through a dust collector, such as shown in Figure 226. The dust collector provides a space wider than the flue, in which therefore the velocity of the gases is reduced, and their carrying capacity correspondingly lessened, so that the dust deposits. Provision is made to feed the dusty gases along the walls on which the dust may

deposit, and to draw the outgoing clean gas from the center, as far from the deposited or falling dust as possible. The dust collects in the cone and may be drawn out at intervals. The dust collector has no moving parts. There are several designs, but the principle is the same for all.
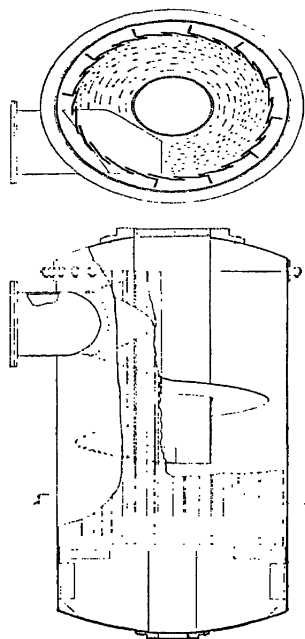
FIGURE 225.—Flick centrifugal catchall and entrainment separator. Entrained droplets pass through the slits of the inner wall, out of the path of the vapor or gas. (Courtesy of Wurster and Sanger, Inc., Chicago.)
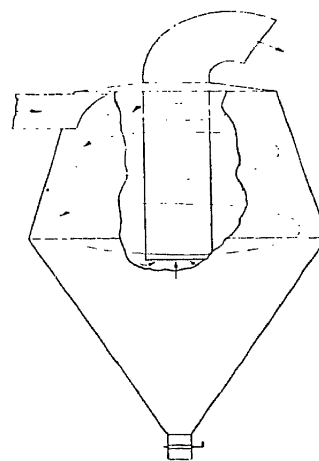
FIGURE 226.—A dust collector.

The Cottrell Precipitator. There are dusts, however, too fine to settle in the dust collector; furthermore, many gases carry fumes, finely divided droplets, or metallic particles just condensing from the vapor state, which no dust box will retain. Until some 20 years ago, there were no practical means to collect the particles in such fumes, but this may now be done by means of the Cottrell electrical precipitator. The gases are passed up a tube in which a copper (or lead-covered copper) wire is suspended; a high-tension direct current passes from the wire to the surrounding tube or pipe; particles of solids present in the gas are electrified by the silent discharge of the central wire, and are then attracted by the pipe, which has the opposite polarity. The gas issues from the top of the pipe free from dust. The effect on mists is the same. The solids deposited on the walls of the pipe are caused to drop off into the

box beneath by rapping. Not only pipes, but rectangular spaces are suitable, with several central wires. A sketch of the single pipe used in preliminary testing is given in Figure 227.

The voltage is used as high as possible, without causing a spark to pass; for the distance of 4 inches, such as that in an 8-inch pipe with central wire, 75,000 volts may be used; for larger pipes, 100,000 volts; higher voltages than the latter are not the practice. Such high voltages
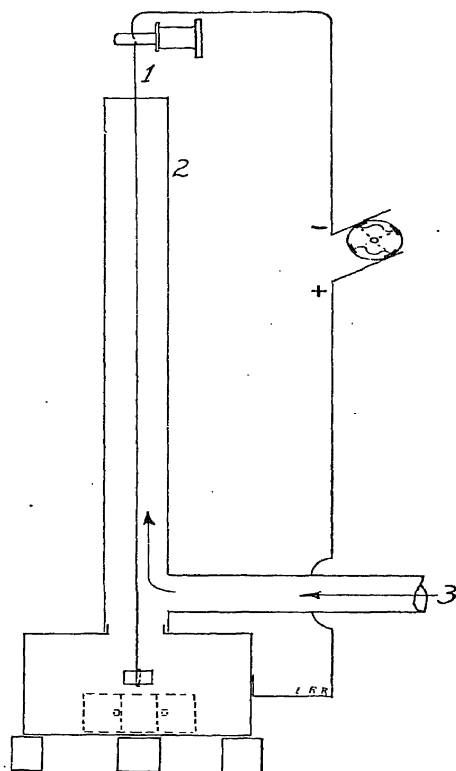
FIGURE 227.—Principle of the Cottrell electrical precipitator. The high-tension direct current passes from insulated wire 1 through the air gap, to pipe 2; the dirty gas enters at 3; clean gas issues at 1. The dirt on the pipe drops into the box below on rapping.

for direct currents are produced in a round-about way; an alternating current is stepped up in an oil transformer (2 coils laid in oil), and mechanically rectified by means of a rotating cross driven by a synchronous motor. There is taken off the rectifying device an intermittent unidirectional, high-potential current, suitable for the precipitating pipe.

For treating large volumes of gases, enough pipes of the standard 15-foot length must be used to lower the velocity of the gas sufficiently to clean it; this velocity differs with the content of suspended solids or mist; an average would be 4 feet per second. A treater may consist of 60 or 100 pipes, which receive the dirty gas below, and deliver to a central flue the cleaned gas at the top; if one treater is not sufficient, a

second one, or a third is installed. For very large volumes, rectangular passages are better suited.

The electrical cleaning of fumes, fogs, and smokes, as it might also be called, has been applied to smelter gases, to sulfuric acid mists, to roasting furnaces, cement furnaces, and other cases. Undesirable gases such as sulfur dioxide are not retained by the treater; but cleaned of solids, the discharge is invisible, and causes less difficulty. In many cases, the material recovered has been salable and has paid for the installation; in other cases, the removal of a nuisance has prevented a shutdown by court order. The quantity of current used is not very great; for 250,000 cubic feet of gas per minute, at 100° to 200° C., the power consumption was 120 kilowatts.[5]

FIGURE 228.—View looking down into Dopp "positively" scraped double motion grease mixer. The scraper makes 15 revolutions per minute, turning on the hollow shaft; the paddles make 25 revolutions per minute in the opposite direction. (Courtesy Sowers Manufacturing Co., Buffalo, N. Y.)
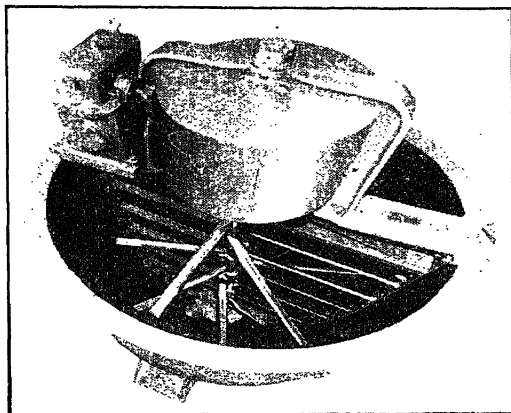
The Magnetic Pulley. The magnetic pulley (Dings[6]) is a device widely used to separate admixed old iron from non-magnetic materials, such as crushed bones, slaughter-house refuse, glass, and many others. The pulley is placed at the turn of a conveyor belt; the bones drop off at the turn, but the iron is carried a short distance along the under side of the belt, to a point just outside the magnetic field; there they drop off in a separate container. The pulley contains coil windings and iron; the coils are supplied with direct current through contact rings protected from dust and brushes (hollow shaft). The pulley may be a driving pulley.

Mixers. A solid may be kept suspended in a liquid by means of rotating arms. In order to mix thick liquids, such as greases, the mixing arms are made to rotate in opposite directions; in general, the vessel used is jacketed, so that heating may be furnished. It is essential to

[5] "Problems in smoke, fume, and dust abatement," F. G. Cottrell, pp. 653-685, in the *Smithsonian Report* for 1913, with 37 illustrations and photographs. The power consumption figure is taken from p. 678.

[6] The Dings Magnetic Separator Co., Milwaukee, Wis. Similar equipment is made by the Magnetic Manufacturing Co., Milwaukee, Wis.

thorough and rapid mixing, as well as to rapid heating, that the walls be scraped. (*See* Fig. 228.)

The Slurry Thickener. A slurry may be thickened by settling it, running off part of the water, and running off to the next operation a slurry richer in solids than the original one. The Dorr thickener is a settler with means for the continuous discharge of the thickened slurry, overflow of the clear water or thinner slurry, and constant feed of the original slurry. It consists of a tank with a bottom sloping toward the center, and 4 arms with plows, rotating slowly so as to drive the thick mud to a discharge pipe; the thin slurry overflows from a point near the side wall and near the top, while the original slurry enters at the center of the top layer.

The Dorr classifier will be found described in Chapter 49, under copper, and will serve as type for classifiers in general.
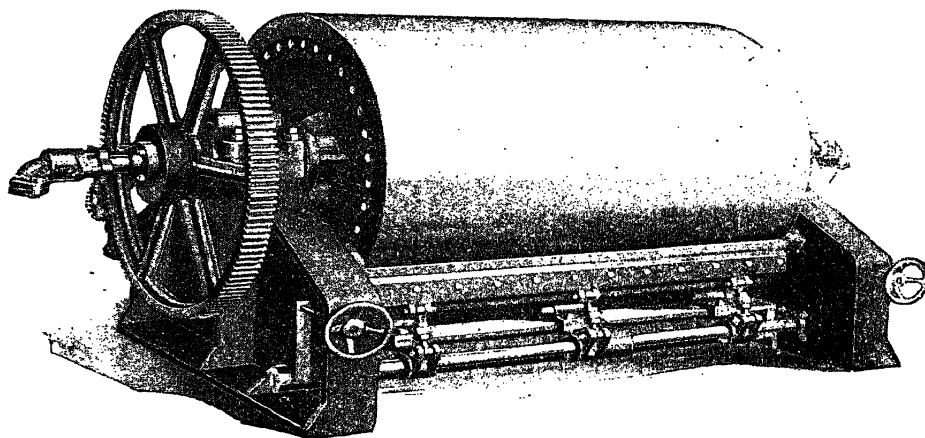
FIGURE 229.—A flaker, or chip machine. (Courtesy Buffalo Foundry & Machine Co., Buffalo, N. Y.)

For rapid settling, or for thickening if the mud produced is not too thick, a tank with several shelves may be used. One such rapid settler or thickener in which any counterflow of muddy and clear liquors is avoided, is the Gilchrist Rapid Settler with parallel flow. The muddy liquor enters down the center; the clear liquor flows out at the upper part of each tray, at the circumference, while the thickened sludge flows down also at the circumference, but in a separate channel from the base of each shelf. The Gilchrist settler has been applied to sugar juices especially.

The Flaker, or the Chip Machine. The production of chemicals in chip form rather than in lump form has been possible by the employment of the chip machine. It consists of a hollow drum, cooled with water (or brine), over which a fused salt is distributed evenly by a small trough at the top and a larger dipping trough at the bottom; the

drum turns at a slow rate, slow enough for the salt to congeal, and the thin solid layer formed is scraped off by a stout knife running the length of the drum; as the layer falls to the movable bin below, it is broken into smaller pieces, easily shoveled into drums, easily dissolved by the consumer, readily weighed out to a given weight, and more uniform in quality. The cylinder may move smoothly, turned by a gear wheel, or it may move by jerks, by means of a ratchet. The thickness of the chips or flakes is controlled by the rate of feed. The main difficulty in some cases is that the layer sticks to the roll so well that the knife does not peel it off readily; there are various remedies, of which one is to place some paraffin in the lower trough. A lower temperature within the drum may also prevent sticking.

Other Patents

U. S. Patent 2,040,431, fractionating apparatus, with 2 figures; 1,889,349, a magnetic separator especially adapted for use in connection with coal crushers; 1,885,717, a magnetic separator especially adapted for separating gold and other magnetic material from sand, etc.; 1,836,252, a magnetic separator; 1,857,884, precipitator, whereby salt or other material, the solubility of which vary with temperature, is precipitated by changing the temperature by means of heat transfer; 1,884,726, an evaporator comprising an upright dome especially adapted for evaporating milk (Kermer); 1,885,402, apparatus for continuous evaporating or distillation employing a vacuum and only a short heating period; 1,907,197, continuously precipitating dust collector; 1,821,842, a dust collector for collecting the dust from grinding, sanding and polishing machines by passing through a chamber containing baffle plates; 1,844,591, dust collector for cement mills; 1,906,534, crystallizing apparatus consisting of a high vertical shell, an agitator within the shell and a means of removing the crystal from the bottom of the shell; 1,860,741, a crystallizer in which a supersaturated liquid is passed upward through a suspension of crystals of substance to be precipitated; 1,810,217, a continuous crystallizer using a helical ribbon conveyor to prevent adherence of crystals to cooling surface as well as carry the crystal and liquor through the crystallizer; 1,884,727, rotary drier in which material to be dried is deposited in a thin film on the periphery of an internally heated drum and then scraped off the drum (Kermer); 1,867,465, a steam drier and means for extracting grit and dust from air; 1,882,405, a rotating drum drier especially suitable for drying silica.

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Frequently the success of a new process depends not upon the correctness of the chemical calculations, but on the proper choice of the mechanical device which brings automatically the raw materials to the reaction chamber, or on the device which takes, automatically again, the product away; for an industrial operation must be profitable or it cannot live. It will be apparent that the importance of an acquaintance with the ordinary mechanical devices which an industrial chemist needs cannot be overestimated.

Chapter 44

Appliances Used by the Chemical Engineer
IV. Crushers, Disintegrators, Pulverizers

The handling of liquids and gases is a comparatively simple matter; its parts push each other; applying pressure at one part brings a quick response from every other; they are of uniform texture; where one part will pass, all the others will. Not so with solids; pressure at one end of a long pipe filled with a solid of assorted sizes would only jam it fast, except for an impalpable powder. Solids must be carried all the way

Figure 230.—The bucket elevator. *F*, feed; *D*, discharge.
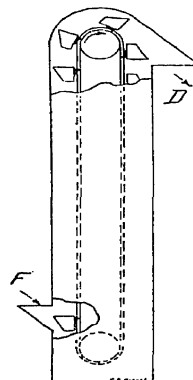
from one spot to another in a wheelbarrow, or in a succession of little barrows or buckets which deliver their load and return to the starting point for another. By making the chain carrying them an endless one and running it over two sprocket wheels, upward and with the load, on one side, and down, empty, on the other, we achieve the automatic elevation of a solid in its simplest form, that of the *bucket elevator;* traveling vertically, it lifts coarse solids to an elevated delivery point. The chain and buckets are enclosed in a steel housing which prevents loss and dust nuisance; the housing has a feed hopper at the bottom, also called the boot; the buckets pass through the solid; a delivery spout is also part of the housing, at the top. The operation is indicated further in Figure 230.

The chain is usually belt-driven; the driving pulley is part of the upper sprocket shaft; the lower sprocket is merely an idler. The buckets are of various sizes, rarely over 4 inches by 8 inches; the travel is slow, about one foot a second, and the capacity rather small.

When a large capacity is needed, an elevator on which heavy barrows may be loaded is used, or a skip hoist.

In the form most commonly used in chemical operations, the buckets in the bucket elevator are at some distance from each other; there are also in use bucket elevators in which the buckets shoulder each other, and cover the chain completely. The other extreme is a form which has only two buckets, of large size, which are so disposed that one descends as the other ascends; both reach the end of their respective trips simultaneously; this type is called the *skip hoist*. It does not include an endless chain; the bucket is really a small car traveling on inclined rails, which is pulled up the incline by a drum-wound cable. The skip hoist has no casing. It is used, for instance, for lifting ore, coke, and limestone to the top of an iron blast furnace.

The Conveyor. In order to move solids from one point to another on the same level, conveyors are used; among the various types may be mentioned the belt conveyor, made of leather or reinforced rubber; the screw conveyor, usually of metal, and the pneumatic conveyor.

The belt conveyor is well adapted to long trips, that is, 100 feet or more [1]; if the material must travel along one level, then up an incline to an elevated level, and still another distance along the upper level, a belt conveyor in a single piece will give the required service.

The belt conveyor is pulley-driven, and rests on small rollers or idlers; on the up-travel the loaded belt passes over auxiliary idlers placed under its two edges slant-wise so that the edges are turned up slightly; the solids cannot roll off. The speed is not high, perhaps one foot in two seconds, but the capacity may be made high by using a wider belt.

By causing one belt to dump its load on a second one traveling at right angles to it, the material carried is made to turn a corner.

For moving solids along the level only, screw conveyors are used, if the distance is short. They consist essentially of a wide sheet-metal screw fitted to a gutter with rounded bottom; the screw shaft is driven by a pulley; as it turns it pushes the solids along the gutter, until they reach an opening which delivers them to a bin, for instance.

A pneumatic conveyor is used chiefly for elevating solids, for example for conveying loose soda ash from a box car to a steel storage tank placed outside the building and high enough to permit feeding to various dissolvers by gravity. The installation comprises a suction pump protected by a dust collector, an air-tight steel bin, and the suction line, partly steel, and partly of rubber, ending in a strainer which is introduced in the car. The fine powder travels up the pipe until it reaches the bin when it drops, because the velocity of the air drawn in is reduced; the bin is really a dust box. The air travels further to the dust collector

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[1] A belt conveyor four miles long is described in *Chem. Met. Eng.*, **32**, 159 (1925).

which cleans it almost completely, then to the pump. The discharge from the suction pump is to the air, but if there is still dust in it, a second dust collector is placed in the discharge line.

The pneumatic conveyor is used for ashes; they are drawn into an elevated bin from which they can be loaded into dump carts or railway cars by gravity; but for this purpose the skip hoist is more reliable.

Poidometer. The poidometer is a device for the continuous weighing of a loaded moving belt, with regulation of the load. The device is placed at the base of a bin, with a small hopper of its own. The belt rests on a pulley which actuates a beam with weights. The beam in turn actuates the gate from the hopper; if too much material is fed, the pulley is depressed, the beam rises, and the gate drops. The graduation on the scale is in pounds per running foot of belt; a separate device
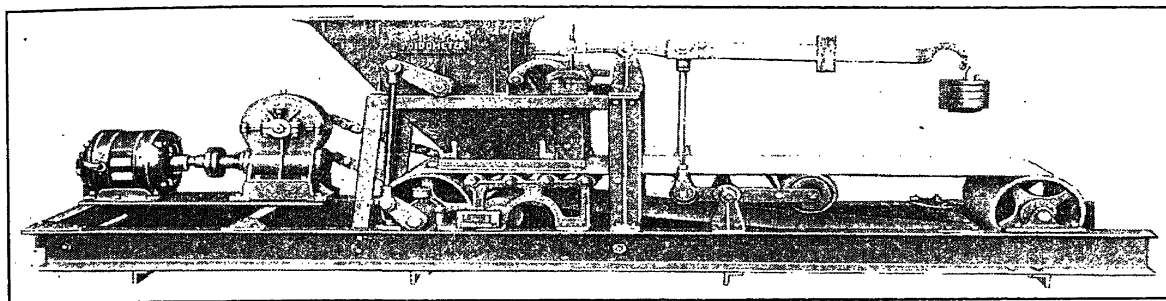
FIGURE 231.—The essential parts of a poidometer. (Courtesy of Schaffer Poidometer Co., Pittsburgh, Pa.)

records the running feet of belt, so that total poundage is automatically recorded, and with proper setting, assured. The accuracy is within 1 per cent. The capacity varies with the size of the poidometer and with the bulk weight of the material; it may be 1 pound per minute or 10,000 pounds per minute.

CRUSHING, DISINTEGRATING, AND PULVERIZING

A distinction is made between crushing, disintegrating, and pulverizing; the lines cannot be drawn with accuracy, for usage differs; for the sake of clearness the distinction will be assumed to be definite. In general terms, crushing means the reduction of large pieces, such as a man can just carry, to egg and nut sizes; the reduction of egg and nut sizes to a coarse powder is termed disintegrating, also grinding; finally, the reduction of the coarse powder to a powder so fine that the separate granules cannot be felt between the fingers is termed pulverizing; these latter fine powders are aptly termed impalpable. The sizes resulting from these operations are never uniform; a mixture of sizes is obtained which must be graded by sieving or screen-

ing; the definition of sizes is then made in terms of the percentage which will pass through a given screen, the remainder being termed "on the screen." Sieves and screens are described by the number of holes or meshes to the lineal inch, if small, or by the dimension of the hole in inches if large; the holes are regular, either circular or square, hence giving the number to the lineal inch defines them. The circular holes are
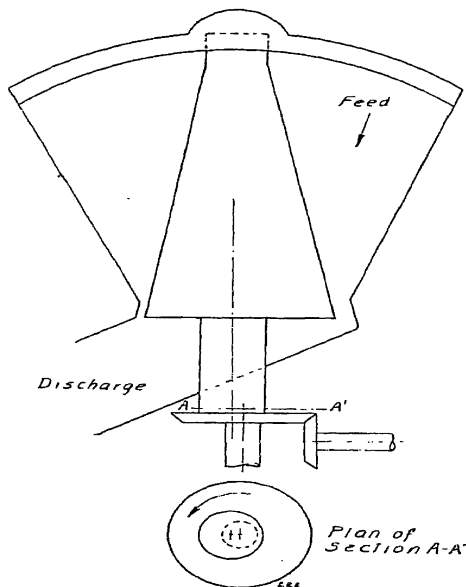
FIGURE 232.—The gyratory crusher, a pot crusher with the rotating element set eccentric to the pot.

made by punching a steel plate; the square holes are made by weaving iron or other wire, and are called meshes.

The distinction above may then be repeated in terms of meshes. Large lumps are "crushed" to pass through a three-inch mesh; "disintegrating" means reducing the size so that 90 per cent, or so, will pass a ten-mesh screen, that is, through a screen having ten meshes to the inch; "pulverizing" means reducing so that 90 per cent, or so, will pass a 100-mesh screen or better, that is, will pass through a screen having 100 meshes or more to the inch.

Crushing is done in gyratory crushers, jaw crushers, and rolls; disintegrating is done in pot crushers, rotary-hammer mills, squirrel-cage disintegrators, and stamp mills; pulverizing is done in buhrstone mills, suction mills, ring-roll mills, pebble mills, and edge runners. There are many other special devices in addition to the ones listed which are used for reducing the size of a solid. Modifications of those given fit them for two classes, but in general the devices are listed as they would come to the mind of a plant man when the three classes of service are mentioned.

The Gyratory Crusher. The gyratory crusher is a pot crusher in which the rotating element is set slightly eccentric to the pot in which it

works. Figure 232 indicates its construction. The rock slides down in the wide opening made at the half-turn when the space is widened; at the next half-turn the space is too narrow to accommodate the piece and it is crushed. The rotating element is grooved vertically. In size the gyratories are built with rotating elements from 3 inches in diameter to 72 inches; the large sizes are the best known. The crusher with the 72-inch rotating element is 45 feet over all, makes 175 r.p.m., and requires 300 to 500 horsepower. It is usually belt-driven; when an unbreakable object finds its way into the pot accidentally, the belt slips and no damage is done to the gears. The large sizes are well adapted to reduce the large lumps brought from a mine or from the quarry, such as gypsum and cement rock, to egg size.

The Jaw Crusher. The jaw crusher has a back-and-forth motion; here too the lump slides down as the space widens and at the next forward stroke is crushed to smaller sizes. It is a powerful crusher; its crushing plates vary in size from 2 by 6 inches to 12 by 26 inches and over. It is most commonly used in medium sizes. To prevent injury when an unbreakable object finds its way between the jaws, a weak point is provided by connecting the moving jaw to the driving shoulder by a slender rod, which breaks, and which is quickly replaced after the foreign object has been removed. The translation of rotary motion to the back-and-forth motion is by means of an oval, mounted on the pulley shaft, as indicated in Figure 233.

The crusher with plates 12 by 26 inches makes 140 complete strokes, that is, back-and-forward trips, per minute; it requires 25 horsepower; crushing to pass 1½-inch mesh its capacity is 12 to 15 tons per hour, half a carload; crushing to pass 2-inch mesh, 20 to 30 tons per hour; the greater capacity of the coarser size is due to the wider spacing between the jaws, which permits more material to pass through.

FIGURE 233.—The jaw crusher.
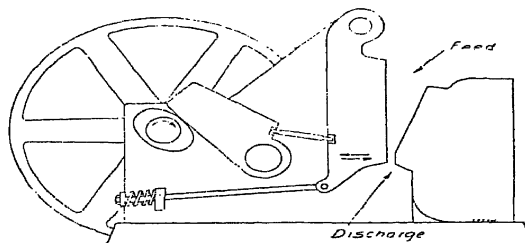
The Rolls. Rolls are used in many sizes, usually double, the rolls rotating toward each other; their surfaces are corrugated or spiked. (Fig. 234.) They are well adapted to materials which crush easily, such as coal, bones, or coke. Provision against destruction is made by mounting one of the two rolls in journal boxes which can be forced back against stiff springs in case an unbreakable object is introduced; through the temporarily widened space, it drops through, and the normal spacing

is made again. Perhaps it should be added that the shafts of the rolls are horizontal, the material is fed in from above, and passes through by gravity. The operation will be clear from the drawing. Instead of two rolls, a single roll working against a fixed plate may be used. The capacity of a roll crusher is high.
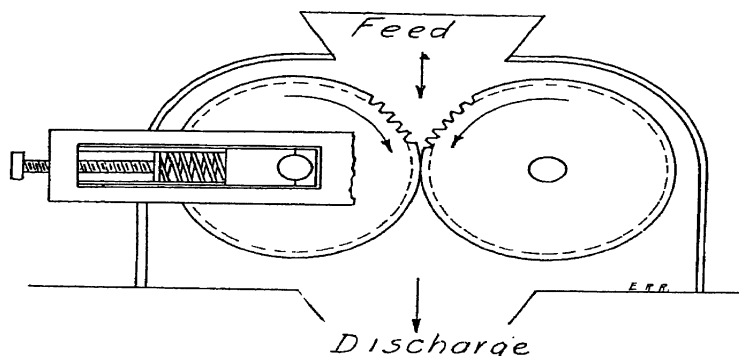
FIGURE 234.—Crushing rolls.

Rotary Hammer Mills. A comparatively new type of disintegrator is the rotary hammer mill, of which there are many variations. The mill shown in Figure 235 is the Jeffrey; it is one of the three best-known examples, the other two are the Williams and the Gardner.

The hammers are steel bars free to pivot on a pin inserted in a central disk integral with the horizontal shaft. As the disk rotates, the hammer is whipped with great force against the incoming lumps; these are caught between the stationary breakers plate, of manganese steel, and the whirl-
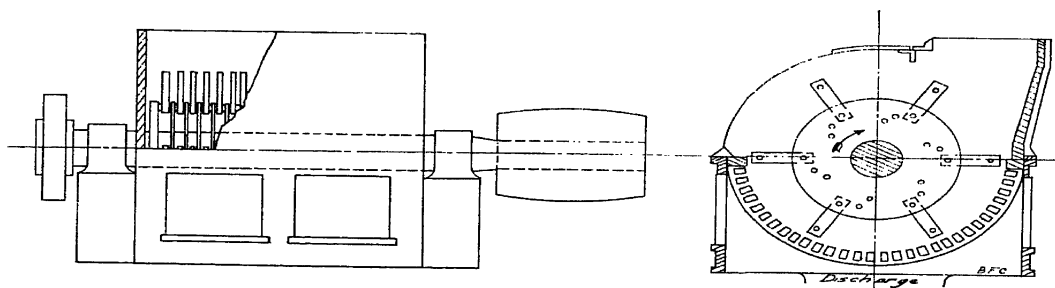
FIGURE 235.—The Jeffrey crusher, illustrating the rotary hammer mill type of disintegrating device.

ing hammers. The solid is reduced to small sizes which pass down through the semi-circular screen forming the lower part of the casing. The speed of the shaft is high, between 600 and 2500 r.p.m., so that to describe the action as cyclonic is rather apt. A long list of materials may be treated in these mills, including asphalt, nitre cake, gypsum,

lime, bone for case-hardening of steel, cottonseed press cake, cinders, clay, and clam shells.

No provision is necessary against unbreakable objects of small size; the hammers can bend back and pass over it; the decreased discharge will reveal that there is an obstruction.

The hammers wear fast; in order to get as much use out of them as possible several holes are provided in the disk, so that they may be moved forward toward the edge as they become shorter; at the stage shown in the figure, they are quite short, and have been moved twice.

The shape of the hammer varies with the use intended; it may be a straight bar, a twisted one, blunt or sharp; it may be a yoke instead of a bar, of manganese steel, free to pivot like the plain bar.

The *pot crusher* is one of the older types of disintegrating device. Its construction is the same as that of the gyratory except that its rotating element is centered, hence the figure of the gyratory will show the principle of the pot crusher. It is still used to some extent.
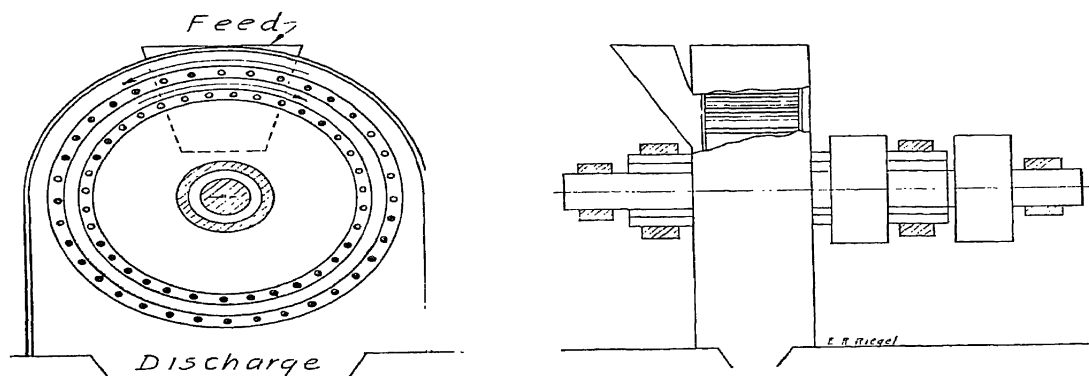
FIGURE 236.—The squirrel-cage disintegrator.

The Squirrel-Cage Disintegrator. In this appliance, two circular cages of steel bars mounted on steel rims, concentric, rotate in opposite directions. The material to be disintegrated is fed in the center, and must pass between the two cages. The lumps are thrown back and forth in the narrow space between the cages until they are small enough to pass through and reach the discharge. The squirrel-cage disintegrator is used to prepare coarse powders, for instance ground nitre cake sold in cans for household uses, such as cleaning sinks and flushing toilets; the powder must not be too fine, and no uniformity of size is sought. The drive is by pulleys; one driving shaft is used; one belt is straight, the other one crossed to reverse the motion. As indicated in the drawing, one pulley shaft is hollow, to permit the second one to pass through. The cages are carried on their respective shafts and these in turn by a steel frame not shown in the figure.

Buhrstone Mill. The *buhrstone mill* is one of the oldest pulverizing devices; it was used by the millers for preparing flour; in the large mills of the Middle West it has been displaced by special corrugated rolls which tend to elongate the wheat kernel rather than pulverize it. In the chemical industries it is rarely used.

Working Fac

Upper Stone   *Lower Stone*
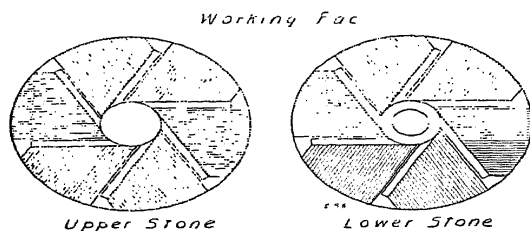
FIGURE 237.—The buhrstone mill.

The Suction Mill. In the suction mill, the material is ground between rotating horizontal wheels of small diameter, thrown by centrifugal force against the inner face of a larger, stationary ring; the material must be so fine that a current of air drawn through the mill can sweep it along as a fine dust; until that fineness is reached, the material remains subjected to the action of the mill proper.

The best-known mill of this type is the Raymond. It consists of the mill proper, a dust collector, and an exhauster. In the mill four smaller wheels are suspended from the arms of the vertical shaft in such a way that they are swinging freely; the centrifugal force presses them against the grinding ring, as shown in Figure 238; here the grinding, or better, pul-

FIGURE 238.—The Raymond mill, illustrating the suction type of pulverizers. *E*, exhauster.

Separator or Dust Collector

Plan of Mill
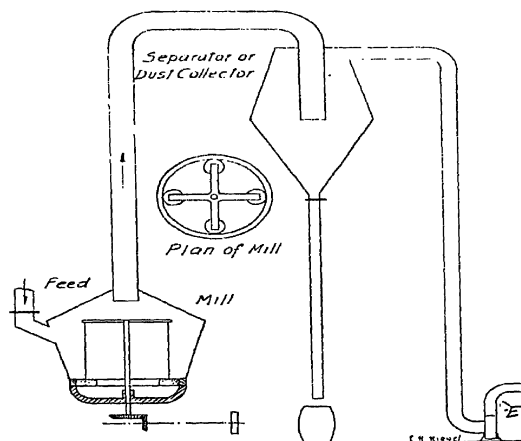
Feed

Mill

verizing, takes place. The speed of the shaft (vertical) is about 100 r.p.m. Air is drawn in through the feed box or through the floor of the mill when connected to the discharge pipe of the exhauster; the fine powder, really dust, is carried up the pipe into the dust collector or separator; here the

velocity of the air becomes very low, since the large cross-section of the box multiplied by a low velocity will give the same discharge as the small cross-section of the pipe multiplied by a high velocity; the dust is deposited, and the air, now free from solids, passes to the exhauster. It is rare that the discharge from the exhauster is free from dust, and that is one reason why this air is frequently led into the mill again, entering below the stationary ring.

The Pebble Mill. The pebble mill in its simplest form consists of a porcelain jar containing a few pebbles; by placing it on the arm of a wheel it may be swung in a circle. As the pebbles glide, the pulverizing process takes place.

One industrial mill is closely modeled after the simple mill above; a steel container, which may be tulip-shaped, replaces the porcelain jar; it carries three or four iron balls for a container 24 inches in diameter. The shaft passes through the long axis of the tulip, and is inclined at an angle of 45°.

FIGURE 239.—A pebble mill for intermittent operation.
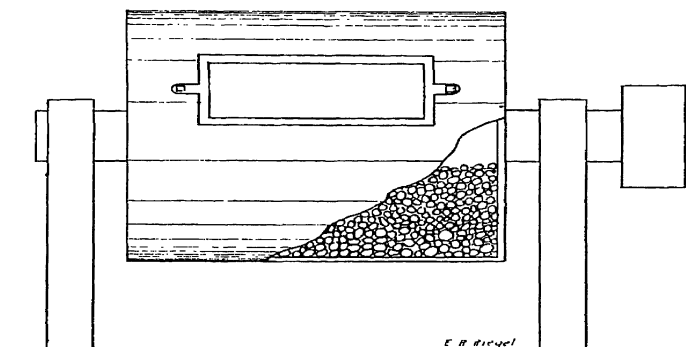
The best-known pebble mill in the chemical industries has water-worn quartz pebbles about $2\frac{1}{2}$ inches in diameter, as nearly spherical as possible; they occupy one-third the space in a hard steel cylindrical container 4 feet long, 4 feet in diameter or larger; revolving on its horizontal axis (*compare* Fig. 239).

A batch of material is placed in the mill, the cover clamped down and the mill revolved at a speed of 60 r.p.m. After a period, the mill is stopped; the cover is replaced by a grid which permits the powder to pass, but retains the pebbles; the mill is revolved again and gradually discharged into the hopper beneath.

This periodic operation may be changed into a continuous one by feeding and discharging through the trunnions; such a mill is the Marcy.

The Hardinge continuous pebble mill is pear-shaped, with the long axis horizontal; the feed (and discharge) is through the trunnions. It revolves at rather higher speed than the cylindrical mill, and has several sizes of pebbles which "classify" themselves; this mill is used for example

for pulverizing Florida phosphate rock after a preliminary treatment in a disintegrator.

A tube mill is a cylindrical pebble mill whose length is several times its diameter.

The Edge Runner. The edge runner is one of the older devices, still much used, but less than formerly. Its function is partly that of a pulverizer, partly of a disintegrator. It consists of two circular stones about three feet in diameter, and eight inches wide, running on the eight-inch face. (*See* Fig. 240.) They are carried on the two hori-
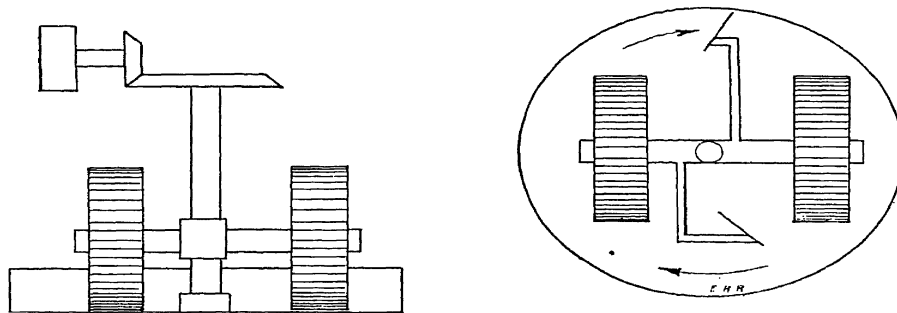
FIGURE 240.—The edge runner.

zontal arms of a vertical shaft, and are placed on opposite sides. As the shaft rotates, the stones are pulled around, and as the line of travel constantly leaves the vertical plane of the stones, there is a side-wise drag which grinds, in addition to the crushing due to the mere weight of the stones. The material lies in a shallow pan; the operation is either batch operation, that is, intermittent, or continuous, by means of slight alterations. Small plows sweep the material into the path of the stones.

Instead of rotating the stones in the stationary pan, the stones may be left stationary, and the pan rotated; also, corrugated steel cylinders of similar proportions may be substituted.

Choice of Appliance and Sequence of Operations

Crushing operations frequently involve two or more devices; for instance, in a coke plant, the coal passes crushing rolls first, and the product is sent to a Gardner crusher, of the rotary hammer-mill type, which reduces the egg size to a coarse powder; this is then loaded into retorts. In a gypsum plant, the rock from the mine passes through the gyratory, then the Jeffrey, and finally the Raymond mill; by these three steps, lumps of rock are reduced to an impalpable powder. Sometimes a single device is sufficient, for instance when sodium sulfide melt is made into cakes about three feet square and six inches thick, such a cake may be broken in several pieces by a sledge hammer, and the pieces fed to a jaw crusher set for rather fine crushing; the product is fine enough for leaching tanks.

The choice of the crushing, disintegrating, or pulverizing device depends chiefly upon the desired fineness, but other factors must be considered. One is the toughness or brittleness of the material; another is whether very few fines are desired, or the greatest possible amount, with few coarser pieces. From any device, a single size is not obtained, but an assortment; to obtain one size, screens are used; the total product of the crusher is run over the screen; that which passes through proceeds to the next operation; that which remains on the screen, the tailings, returns to the crusher.

Screens. For small operations, a hand screen is used; it may be made by tacking a wire netting to a four-sided wooden frame. Placing the material in it and moving the whole mass back and forth, a part of the solid will pass through and a part will remain on the screen, if properly chosen. In all screening operations of the automatic type, some motion
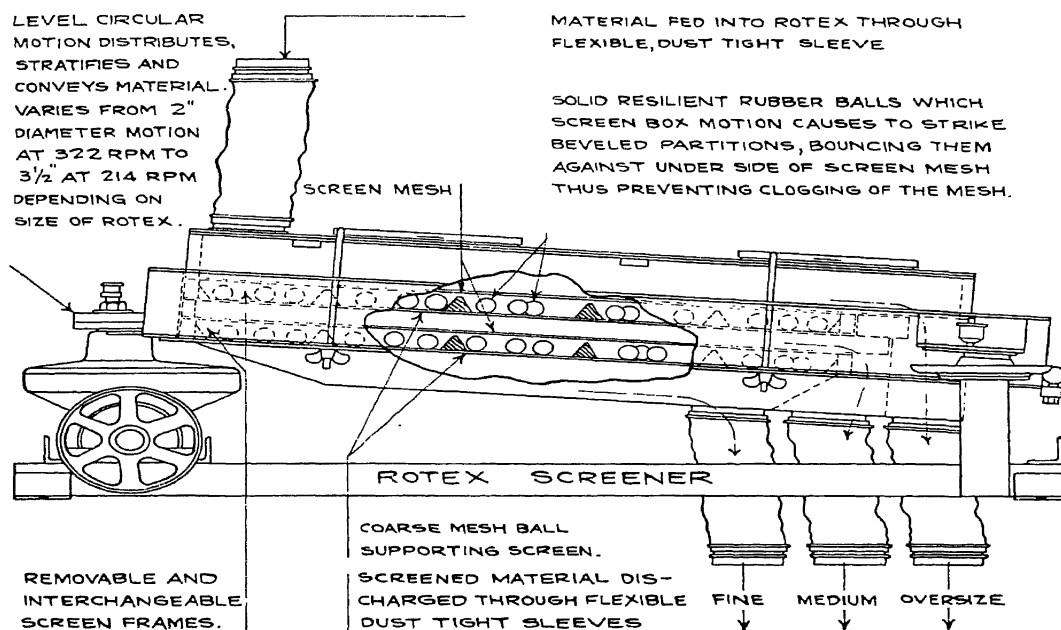
FIGURE 241.—Flat screen with rapid rotary jerky motion, and with tapping.
(Courtesy Orville Simpson Co., Cincinnati, O.)

is required, otherwise the mass lies on the screen and clogs it. Some automatic screens achieve this motion by revolving and so moving the solids; others are inclined, stationary, but receive rapid blows which constantly dislodge the material, causing the tailings to roll down the incline. The Newaygo screens of the Sturtevant Mill Company are of this type. Usually three sizes are sorted by means of two screens, the coarser screen being placed over the finer one. The fines pass both screens; the middlings pass the upper but not the second; they run to the low point where a

chute or a screw conveyor transfers them to the next device; the tailings cannot pass either screen and are returned by means of a chute and a bucket elevator to the disintegrator. The screens are always placed below the mill, so that they are fed by gravity; they are mounted on steel frames with cross members; the vibration is imparted by small hammers driven by cam shafts.

A different principle is involved in the Raymond mill, which requires no screen at all; the material is graded entirely by its lightness in a current of air (or other gas). The Rotex screen is exhibited in Figure 241.
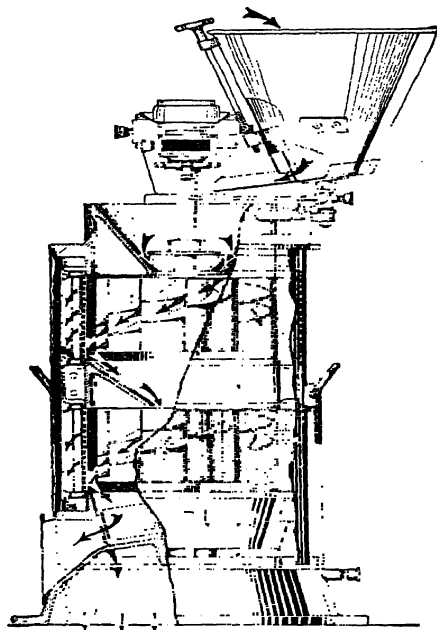
FIGURE 242.—The Blutergess high-speed turbine sifter. (Courtesy Abbé Engineering Co., N. Y.)

In the Blutergess high speed turbine sifter, a still different principle is applied. There is no shaking, no vibrating, no suction. The material is thrown by a central turbine against the cloth. (*See* Fig. 242.) The motor is $1\frac{1}{2}$ h.p.; the surface of the stationary screen is $6\frac{2}{3}$ sq. feet; yet the capacity is high. With a speed of 740 r.p.m., and a 110-mesh screen, 550 pounds of precipitated sulfur are screened per hour. With 1400 r.p.m., and a 60-mesh screen, 2000 pounds of aluminum stearate are delivered through the screen per hour. Two sizes are produced: the screened size, and the tailings.

The *rotary screen* may be cylindrical, of the same diameter throughout, when it is usually given a slight incline toward the discharge end. It is mounted by slender arms to a central shaft, which is rotated slowly.[2] The material is fed to the inside of the screen; as the screen rotates, the

[2] About 6 r.p.m. for a screen 36 inches in diameter and 140 inches long.

solid travels further and slightly down; the fines pass through the meshes. If the screen has two sizes, the smaller mesh is first; using hypo crystals as an example, the fine powder would pass through first, the pea size and the lumps would roll on. At the second size mesh, the pea would drop through and would collect in barrels, free from either fines or lumps. The lumps pass all the way through the cylinder, and drop off at the lower end.

Instead of being cylindrical, the screen may be wider at one end than at the other; the material enters at the narrow end, and as the screen rotates around its horizontal shaft, it moves downward toward the wide end, where the tailings are discharged. Such screens are used for heavy materials such as gypsum rock or pyrite.

OTHER PATENTS

U. S. Patent 1,859,499, rotary drum ball mill in which pulverized material is removed by a current of air or fluid; 1,879,479, ball mill for carrying out reactions in the nature of sulfur fusions; and 1,862,557, same; 1,840,380, pulverizer of the rotary beater type; 1,862,889, a rotary crusher with screening grid; 1,888,636, cylindrical screening and concentrating apparatus having rotary motion; 1,882,908, inclined vibrating screen; 1,819,049, horizontal rotary screen or trommel; 1,798,433, rock crusher having an eccentric operating mechanism, and a shaker screen having its receiving end mounted on the eccentric of the crusher; 1,884,316, crusher of the rotary type applicable to furnace constructions; 1,874,830, jaw crusher consisting of a movable and a fixed jaw; 1,872,233, hammer mill crusher; 1,847,859, a double roll crusher; 1,871,727, apparatus for disintegrating particles suspended in a liquid; 1,764,138, hammer mill which has a series of hammers which crush the material as it moves along on a belt (does not have cage bars); 1,762,727, grain disintegrating mill consisting of one movable and one fixed attrition plate.

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"Principles of chemical engineering." W. H. Walker, W. K. Lewis, and W. K. McAdams, New York, McGraw-Hill Book Co., 1927.

"Chemical Engineering Catalog," issued annually by the Chemical Catalog Co., Inc., New York, should be consulted for general information on available appliances described in the Chapters 41 to 44.

"Crushing and grinding," W. F. Carey, *Trans. Inst. Chem. Eng. (London)*, 12, 179 (1934).

"Crushing and grinding appliances, the connection between type and purpose," B. W. Holman, *Trans. Inst. Chem. Eng. (London)*, 12, 186 (1934).

Among the many tasks which devolve upon the chemical engineer is that of finding vessels in which the reactions of commercial importance may be run. The requirement is never that the vessel should last for many years, but merely long enough so that its cost may be absorbed by the process; it follows that a cheaper vessel may be replaced more often than a dearer one, and that a valuable product will permit a more expensive reaction vessel than a product selling for a low price. A second consideration is that the time lost for replacement must be as short as possible, for while the plant is idle it earns nothing.

Chapter 45
Materials Used by the Chemical Engineer

The materials used by the chemical engineer are very numerous; of first importance are steel, cast-iron, wood, stone slabs, bricks of various kinds, lead, copper, and stoneware. These materials serve for the construction of reaction vessels, absorbing and collecting vessels. The subject of bricks has as an inseparable part that of the cement in which they are laid; the cement must resist the attack of the reaction mass as well or nearly as well as the bricks themselves. Of secondary importance in point of tonnage are the special alloys such as duriron, monel metal, bronze, quartz, glass-lined cast-iron vessels, and others. A third class of substances are the filling materials in towers for the absorption of gases in water, or for the drying of gases by means of sulfuric acid for example. A fourth class might be that of the catalysts, such as platinum and iron. A fifth class are the absorbents, such as charcoal in the Burrell process for the removal of gasoline from natural gas. All these classes are used by the chemical engineer; the divisions are for the sake of clarity chiefly. But besides making the material, it must be shipped, and suitable containers are essential for the full development of a manufacture; glass, lead, steel, wood, absorption in diatomaceous earth, even wax, are concerned in the development of shipping containers.

Unlined steel is used wherever possible; storage tanks of considerable size are built of mild steel sheets, riveted or welded; the sheets with proper curvature and with the rivet holes punched, are shipped by rail and assembled on the spot, so that there is no limiting size in transportation which interferes. With cast-iron, it is different; unless the piece is made in sections, bolted together on the job, its size is limited by the size of the railway cars. Unlined steel is used for the storage of oil, ammonia liquors, alcohol, concentrated sulfuric acid, mixed acid, and oleums, besides countless other liquids; it is the reaction vessel for the recovery of ammonia from the ammonium chloride liquors in the Solvay soda process, for the distillation of industrial alcohol and methanol, for the soda wood-pulp digester, and many others. Cast-iron is used for caustic [1] pots, for the

[1] References to other chapters would be so numerous in the discussion of materials used by the chemical engineer that they will not be given; the reader will please consult the list of chapters at the front, or the index.

final concentration to the anhydrous condition over the free flame; for nitric acid retorts, and Mannheim furnaces for hydrochloric acid; for the nitration and sulfonation of benzene and other organic substances; and for many other reactions. Cast-iron is not as strong as steel, and must be heavier as a result, but it has the great advantage that it can be cast to any curved shape desired, and the curved surface is free from joints. The casting may be water-cooled and inside channels so arranged that the desired circulation is obtained. Castings are comparatively cheap.

Castings (Iron). In a foundry, pig iron is the main raw material; it is chosen of a specific quality, and a certain definite proportion of steel scrap is added which among other things lowers the carbon somewhat. The pig iron with added steel is melted in a cupola, essentially a small blast furnace with an hourly capacity of 10 to 15 tons. The fuel is coke, and a small amount of flux (limestone) is provided, whose function it is to form a slag with the ash from the coke and any sand adhering to the pigs. The iron passes through the cupola practically unchanged in composition; the carbon, combined and free, remains the same; the silicon decreases somewhat, the sulfur increases slightly. The loss in iron is 5 per cent, chiefly as globules mixed with the slag.

The melted iron is drawn into ladles carried by overhead cranes (electric), and poured into the prepared form. Small castings are made in "flasks", two-piece boxes filled with sand in which the impress of the design is half in one part, half in the second part; the inner part of the casting which is to be hollow, is represented by a solid shape of sand, the core; where the core is, the metal cannot flow; it can only fill the space between the core and the flask. Flask and core are made from a pattern made of wood, from accurate measurements, with enough oversize to allow for the shrinkage of cast iron on cooling, one-eighth inch per foot. The small castings are poured from a crucible on long bars carried by two men; the crucible is filled from the ladle. The core is made to hold together by moistening the sand with molasses and baking till hard.

The practice in making a casting may be further illustrated by a caustic pot, which is cast right side up, that is, with the flange on the top and the round bottom at the base. There is first constructed a core, which is so large that bricks as well as sand are employed; around the core, a mold provides the outer wall which determines the outside surface of the casting. An extra height is provided in which the metal rises, carrying in its upper portions any slag which it may contain (the riser); this part is later sawed off. The metal flows into the comparatively thin space so provided, and fills it. After some cooling, the outer wall pieces are knocked down or lifted up (annular shapes); the pot may then be lifted in turn, and then the core knocked out.[2]

Castings are cleaned of core sand by sand blasting or by wire brushing, and may be machined on lathes; they may be drilled and threaded.

[2] *Compare article in Chem. Met. Eng.*, **20**, 394 (1919), with 8 illustrations.

Cast-iron drillings are short, almost powdery; steel drillings are long spirals or shavings.

Steel. The steel used for storage tanks, car tanks, stills, reaction vessels, settling tanks, classifiers, evaporators, and an endless number of purposes is generally mild steel, with 0.20 to 0.30 per cent carbon. The thickness varies with the size of the vessel and the purpose. For a storage tank for alkaline liquor, 20 feet in circular diameter and 20 feet high, the sides would be three-eighths inch, the bottom perhaps one-half inch in thickness. Steel tanks are riveted, single or double, and caulked by a pneumatic chisel. The practice of welding instead of riveting is growing constantly; the weld has the advantage that it does not need caulking, and is not subject to a leaking rivet. Steel tanks exposed to the weather are painted on the outside.

Steel may be punched, as well as machined; it may be drilled and threaded; it may be bent into box-like shapes, cutting for the corners and welding the edges; two such boxes, one shallow and one deeper, are riveted together to form a jacket through which water may be circulated, the water-cooled jacket, suitable for furnace walls without any protection. Inhibitors of corrosion are briefly mentioned in Chapter 1 (*see also* reading references there). The suitability of steel to certain strengths of sulfuric acid will be found discussed in the same chapter.

Wood. Formerly wood was used much more than now; it is frequently replaced by steel. For some processes, in which dilute mineral acids are used, wood (oak) is still the best material; for example in the extraction of bones with cold dilute hydrochloric acid for gelatin and glue making. For intermediate water storage in large plants, wooden tanks are freely used. A wooden tank is made tight by swelling it with water, and it will remain tight if kept filled; but if allowed to become dry, the planks shrink, and leaks develop; in this respect the wooden tank is inferior to the steel tank. Wooden tanks lined with lead are used for storage, crystallizers, and other purposes.

Stone Slabs. Towers for the cooling of hydrogen chloride and for its absorption in water to form hydrochloric acid may be constructed of stone slabs. Sandstones about 6 inches thick and 4 or 6 feet square are placed for several days in hot tar which penetrates into the stone a short distance and renders it acid-proof; a stone 7 feet square 12 inches thick forms the base; it is hollowed out enough to give drainage to the discharge opening at its center. The bottom stone is placed on piers, and the square tower is built up of the thinner stones, each course consisting of two 4 by 4 and two 6 by 4 stones, held together by cast-iron corner pieces and steel rods. The joint between the stones may be filled with asbestos cord, or with specially made rubber gaskets. Such towers are not used as much as formerly, but many are still in operation. Every Mannheim furnace has at least a cooling box for the gas made of tarred stones.

Bricks. The common red brick and the sand-lime brick are used for piers and outside courses; soft or hard firebricks for the lining of

fireplaces. The latter are also the more common acid-resisting bricks; they are strong, hard, and tough, and unaffected for example by the acid liquor in the sulfide pulp digester. In this digester, the bricks are laid in litharge and glycerin for cement; this mixture hardens and resists the acid liquor as well as the bricks. Until its introduction, the digesters had to be relined at frequent intervals, a costly interruption. In fireplaces, the bricks are laid in moistened fire clay, or in fire clay and silicate of soda solution. Sand and silicate of soda is also useful, and sometimes for filling cracks between bricks in a hot furnace (with alkaline charge), sand alone; it is gradually fused by the alkali and runs into the spaces between the bricks. Portland cement with sand is used in the outside courses, unaffected by the furnace charge, but may also be used in numerous cases inside the furnace. Ground asbestos in silicate of soda is both fire-resisting, and to a considerable extent acid-resisting; for nitric acid, a little linseed oil is incorporated. Some silicate of soda mixtures protected by trade names contain, besides ground asbestos and silicate of soda, some tar. "Acid-proof" cement, sold as special cement under that name, is usually ground flint, which the customer is directed to mix with silicate of soda solution; fire clays and ground asbestos may be equally suitable.

Portland cement furnaces are usually lined with bauxite bricks, while magnesia bricks for basic Bessemers and similar processes are very resistant to slag and fused limestone. Chrome bricks are as dear as magnesia bricks ($100 to $200 per thousand); they are said to be neutral; slag does not cling to them.[3] Somewhat cheaper alkali-resisting bricks are made from alunite.

The function of all the bricks given above is to resist heat and chemicals; a brick may be needed, however, for a totally different purpose, namely, to divide a heating chamber from a reaction chamber; in this case, it may still need to be heat-resisting, but it must also be reasonably heat-conductive. Silica bricks are such, discussed in Chapter 10, where crucibles are also discussed.

Lead. It may be said that it is to lead that the chemical industries owe their success; until it was employed for the reaction vessels in the manufacture of sulfuric acid, the latter product was a curiosity; it is now a commodity at 1 cent, in favorable cases 0.5 cent per pound, and even less. Lead sheets form the walls of the sulfuric acid chambers, of the Gay Lussac and Glover towers, of the storage tanks, with wooden or steel frames, for the piping of the acid, for pumps, and for the conveyance of the gases from one tower to another perhaps distant one. The lead chamber walls are supported on wooden (also steel) frames, and the sheets are burned together, that is, the edges are melted together with a hydrogen-air flame. Lead-lined steel is used for the saturation of soda ash suspension in the manufacture of anhydrous bisulfite of soda, for the pickling bath in the galvanizing plants (if sulfuric acid is

[3] In normal times, a firebrick good for 2600° F. costs about $47; good to 3200° F., $85 to $100; size in both cases 4½ × 9 × 2½ inches; silica bricks, $58 and over. All prices for 1000 bricks, f.o.b. brick yard. Fireclay costs $9.80 per ton (for bulk).

the pickling acid), in ammonium sulfate saturators, and in numerous other installations. Lead sheets which have become perforated, or thin in spots, are sent to be rerolled for a nominal charge, into any thickness desired.

Lead used for chemical purposes such as those listed above is not the purest lead, but contains antimony, copper, zinc, and other impurities which render it more acid-resisting. By raising the antimony content to 6 or 10 per cent, the lead is made rigid, about twice as strong as chemical lead, and remains acid-resisting. For many purposes, however, it is an advantage to be able to bend a pipe line at will while laying it, and in general, ordinary chemical lead has retained its primary position.

Copper. Copper is used for the redistillation of acetic acid, which does not attack it except to a slight degree; copper is used also for the steam coils in crude methanol stills, and for the rectification of some of the crude fractions. Copper is the melting vessel for a number of copper alloys, and in the manufacture of varnish. Shelves and trays in the fractionating towers for liquid air, as well as for bubble towers in oil refining, are made of copper. Water-cooled copper coils are used in electrolytic furnaces, while water-cooled copper or copper alloy discharge pieces are suitable for fused sodium sulfide and other furnaces.

Stoneware. For acid vapors and acid liquors, stoneware furnishes cooling, absorption, and collecting vessels; it is made of selected clays, screened of all coarse particles, and sintered throughout its thickness; a strong material results, which may therefore be thin (one-half inch) and correspondingly more elastic and more efficient in cooling action. For mere storage, with no temperature changes, the vessels are thicker. Some further information will be found in Chapter 10.

Hard Rubber. Hard rubber piping, pumps, and pistons have been applied with success in a number of cases; as example, hydrochloric acid may be pumped from one place to another one-quarter mile away by means of a small hard-rubber power pump and hard-rubber piping. Hard rubber may be threaded, and the threaded pipes put together with unions and sleeves; still another advantage is that hard rubber may be softened by hot water. It remains unattacked by almost any acid; hydrofluoric acid does not attack it.

Duriron. Duriron is a cast iron with abnormally high silicon content, namely 14 per cent; it is practically unaffected by sulfuric or nitric acids, and only very slightly by hydrochloric acid. The drain pipes from sinks in large laboratories are made of duriron, which resists completely the action of the dilute solutions of all kinds of chemicals. Complete nitric acid condensing plants made of duriron (Hough patent) are in use, and generally the first cooler in any nitric acid plant is made of duriron, for this material has the passivity of stoneware combined with almost the strength of cast iron, and a thermal conductivity surpassing that of stoneware and approaching that of cast iron. Acid lines are frequently duriron, and in general, this alloy has been a boon to

the chemical industries. Tantiron and Corrosiron are essentially similar high-silicon cast irons, and serve similar purposes.

Duriron is extremely hard and brittle; it must be reinforced in many instances by a cast iron or steel envelope or frame. Duriron cannot be machined, drilled, or threaded; in order to face two flanges so that they fit they must be ground with abrasives, a tedious and expensive process.

Monel Metal. This white metal contains 67 per cent nickel, 28 per cent copper, and 5 per cent other metals, but no zinc, tin, nor antimony. it melts at 2480° F. (1360° C.), higher than cast iron or copper (specific gravity 8.87 cast). It is unaffected by common salt solution, while cast iron, steel, and copper are attacked. With many other chemicals it is comparatively inert, although it does not resist acids as well as duriron does; but monel metal has the great advantage that it can be drilled and tapped, and in general handled in the machine shop as steel is. It may also be cast. The tensile strength of monel metal is greater than that of mild steel and equal to that of medium steel.[4]

Monel metal may be drawn into wire, and this woven into cloth which may be used in the filtration of alkaline slurries, for which iron wire cloth is usually employed; in such cases the monel metal wire cloth lasts several times as long as the iron wire cloth.

Monel metal is much more expensive than steel, but in spite of this, its use has been expanding. Rotary driers for salt [5] (NaCl) have been lined with monel metal plates, held in place by bolts of the same material. In refrigeration plants, all parts which come in contact with the brine give better service if made of monel metal. For the handling of sea water (on board ships) it is made into pump linings and pump rods; propellers of all sizes have been made of monel metal.

Chromium Alloys. Chromium steel and iron find several important applications in the appliances of the chemical engineer. The alloy consisting of iron and 13 per cent chromium resists the corrosion of water, salt water, and a great number of other liquids; it is often called stainless steel. It serves in the form of pipes, valves, autoclaves, and other containing vessels, also in making cutlery. As an example of the wide range of possibilities, it might be stated that the 14 per cent chromium alloy with 0.15 per cent carbon resists nitric acid of any concentration at any temperature below the boiling point; it has been found suitable as the structural material for reaction and absorption towers in the ammonia oxidation process to nitric acid.

Not only the chromium-iron alloys, but chrome-plated steels are very resistant to corrosion, so that chrome plated pieces of large sizes are now used by the chemical engineer. As example, the vaporizing chamber in the Dubbs process for cracking oil for gasoline might be given. Plated tableware and automobile fixtures are very beautiful, with a high luster

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[4] For tensile strength of steel, *see* Chapter 48; monel metal has 90,000 pounds per square inch, for tests on rods (booklet on Monel Metal, by the International Nickel Co., New York).

[5] Fifty-five feet long, 6 feet diameter.

and a bluish color; they do not tarnish. A number of alloys are described in Tables 73 and 74.

TABLE 73.—*Composition and Corrosion-Resistance of Some Chromium Alloys.**

Alloy	Composition	Resists
Allegheny metal	Fe; Cr 17-20; Ni 7-10; Mn $<$.5; S $<$.5; C $<$.2	H_2S, SO_2, oxides of N, HNO_3, NaOH, NH_4OH
Duriron (not machinable)	Fe; Si 14.5; C .85: Mn .35	H_2SO_4, HCl, HNO_3, HAc, NaOH, NH_4OH, Cl in Aq. sol.
Elcomet K	Ni 22; Cr 23; Cu 3.5; Mo 2; W .13; Fe 48; Si 1.25; Mn .50; C .12	Corrosive mine waters in coal mines; any acid liquor.
R-55 (La Bour)	Ni 52; Cr 23; Cu 6; Mo 4; W 2; Fe 8; Si 4; Mn .50; C 25	Viscose solution in rayon plants.
Hastelloy A	Ni 60; Fe 20; Mo 20	Dil. cold H_2SO_4, dil. cold HCl, HAc, NaOH, NH_4OH
Nichrome	Ni 60; Fe 25; Cr 15	
Stainless A	Fe; Cr 14; C .35	HNO_3, HAc, NaOH, NH_4OH
Stainless N	Fe; Cr 18; Ni 8; C .18	HNO_3, HAc, NaOH, NH_4OH
Stainless steel	Fe; Cr 8 and over; Mn 4; C $<$.12	HNO_3, HAc, NaOH, NH_4OH
Stellite (not machinable)	Co 40-80; Ni 0.25; Cr 20-35; C .75-2.5	H_2SO_4, HAc (in absence of air), NaOH
Monel metal	Ni 60-70; Cu 25-35; Fe 1-3; Mn .25-2; C .5-3	SO_3, NaOH, HCl, H_2SO_4
Zirconium #200	Zr 2.77; Si 9.15; Ni 71.41; Al .32; Fe 12.03	

Chem. Met. Eng., **36**, 584-5 (1929).

Fused Quartz. A material totally unaffected by acid gases is fused quartz, obtainable in many forms, among others in 4-inch diameter S-bends, suitable for the cooling of hydrogen chloride. Other shapes are recommended as absorbers of the same gas in water. Quartz pipes withstand changes of heat better than stoneware, and are used for a

TABLE 74.—*Corrosion Tests on Special Material for Comparison with Zirconium Alloys.†*

Sample	C* in 5 per cent HCl Aerated	C in 95 per cent H_2SO_4
Duriron	....	0.00002
Cast steel	0.04468	0.00817
Cast iron	0.16298	0.00004
Hastelloy A	0.00437	0.00001
Zirconium, #200	0.00366	0.00006

† Taken from "Corrosion resistance of zirconium alloys," H. L. Coles and J. R. Withrow, *Trans. Am. Inst. Chem. Eng.*, **27**, 253 (1931).

* C = Corrosion expressed as inches penetration per month.

first cooler (in the Mannheim) with good results, but otherwise its service is not markedly superior to that of stoneware, which is far cheaper. Quartz is furthermore easily broken by an accidental blow.

Figure 243.—A "Pyrex Glass" fractionating column.

(Courtesy Corning Glass Works.)
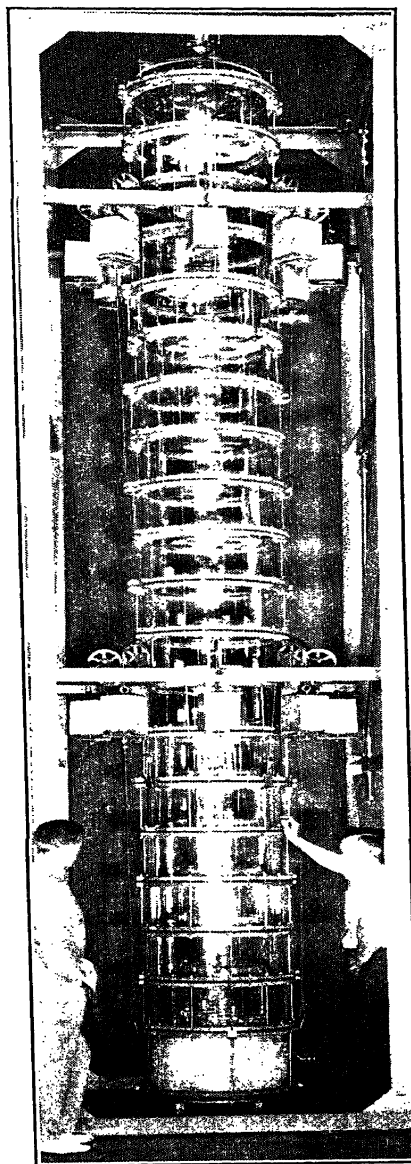
For the preparation of chemically pure water, a quartz apparatus is well adapted.

Pyrex Glass by itself, and not merely as a lining, is fast taking a prominent place among the materials available to the chemical engineer. The adjoined figure shows an all-pyrex distilling column; the advantage of being able to follow the operations with the eye will be evident. The

bells on the several plates are fastened down with pyrex bolts and nuts.

Glass-lined cast-iron vessels combine the inertness of glass with the strength of cast iron; they are used for numerous evaporations and reactions. For the preparation of yeast cultures brass-lined tanks are indispensable. For many purposes, fair-sized enameled and glazed porcelain vessels may be improvised from slightly defective (in shape) bathtubs, rejected for the regular trade.

Sulfur-containing cements, melting at a moderate temperature, may be flowed over the inside of a cast-iron vessel coating its walls, so that it becomes acid-resisting, for cold acids (basolite).
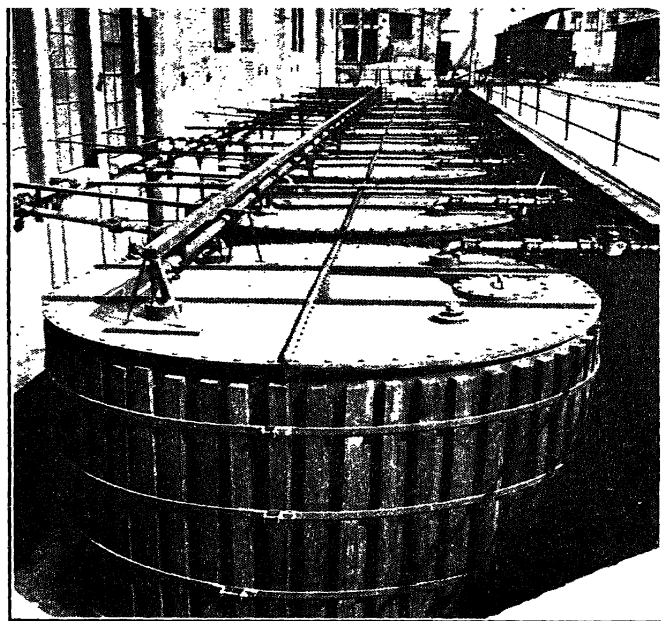
Figure 244.—Storage tanks for 40 per cent hydrochloric acid made of Haveg, reinforced by outside wooden strips. (From the Bergius plant for Wood Hydrolysis, Heidelberg.)

A material called *Mammut,* of German origin, has become of importance in the wineries, for coating the inside of wooden tanks as well as concrete ones, in which the grape juice and the fermented product is held. Mammut is black, resembles wax in appearance, is tasteless, almost odorless, and insoluble in the dilute alcoholic and acetic wine solution. The faint odor which it has is that of an odoriferous balsam.

A newcomer among the structural materials, *Haveg,* a phenolformaldehyde type resin containing a selected asbestos filler. It is a strong material, and has the particular merit of resisting most acids of low and medium concentrations. Specific gravity, 1.6; compressive strength 10,400 lbs./sq. in.; unchanged in any way up to 130° C. (265° F.). It has a low heat conductivity. Haveg is made into tanks 10 feet high and 10 feet in diameter. Tanks for pickling iron, for electrolytic proc-

esses, for dyeing operations, are available of Haveg. In many cases, a steel shape is covered with the resin and filler, combining the strength of steel with the inertness of the resin. Haveg does not resist acetone, strong oxidizers, pyridine, or sodium hydroxide.

Tower Packing. For the absorption of gases in water, towers may be packed with coke in many instances, an inexpensive packing. Broken stoneware may be used, or the special trays such as the Lunge towers for nitric acid gases. For sulfuric acid, quartz lumps, with irregular shapes, and classified as to size, are used. Hollow spheres of stoneware have been proposed, while the so-called spiral chemical rings, in two sizes, 6 and 3 inches in diameter, have been very successful.[6] A good

FIGURE 245.—Diatomaceous earth, from New York state, showing the fine structure which gives rise to large surface; run of mine sample, unselected. Micrograph as reproduced, 62 diameters. (Photographed in author's laboratory.)
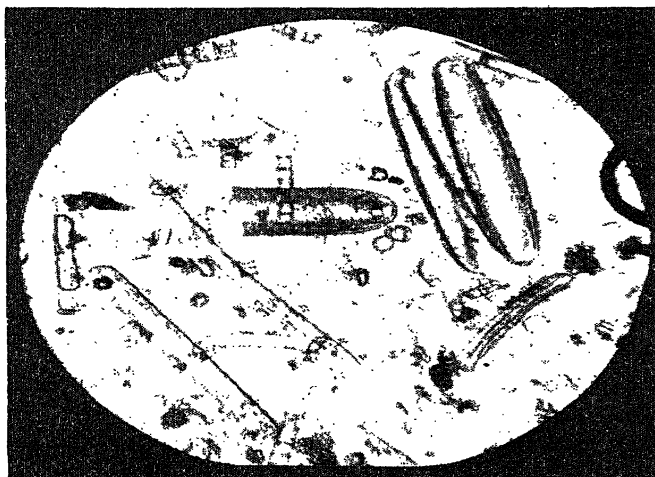
packing must offer maximum surface of the liquid to the gas, retain the descending liquid for a period long enough for saturation, and allow free circulation of the ascending gas.

Catalysts and absorbents are discussed in their proper place in other chapters. The science of catalysis is rapidly advancing, but as yet many firms must make their own catalysts, because some of the catalysts are not as such on the market, even in a preliminary form. As absorbents, charcoal and silica gel are best known; both have been applied to the removal of valuable gasoline vapors from natural gas. Silica gel is made [7] from silicate of soda solution (sp. gr. 1.185) by the action of hydrochloric acid (10 per cent), at the temperature of 50° C., with stirring. After setting 4 hours, the gel is washed free from salt with water and dried in a current of air at 75° to 100° C.; finally heated in a vacuum. Hard, transparent, porous granules result with high adsorptive power. The gel is stable to 700° C. Only by observing certain

[6] Manufactured by the B. Mifflin Hood Brick Co., Atlanta, Ga.
[7] U. S. Patent 1,297,724 (1919), to Walter Patrick.

definite conditions is the gel obtained in the active form, with high commercial value. Activated alumina is a partially dehydrated aluminum trihydrate, which can absorb as much as 14 per cent of its weight in gases and vapors. As for silica gel, the alumina absorbent must be reactivated by heating, to 350° to 600° F., followed by cooling before starting the next cycle. Activated alumina is furnished in granules which pass an 8 to 14 mesh, and other sizes. Silica gel is furnished in a similar size granule, and also for certain absorptions, in powder form.

Aids in filtration in the form of fine powders, usually natural powders such as diatomaceous earth, have been introduced under various names (Silocel) and have proved of great help; they are stirred into the turbid liquid, and after some time the filtration is performed. The very fine, essentially colloidal particles of the turbidity are adsorbed by the added powder. The same powder frequently removes color as well as turbidity, but not always; with oils, such as linseed oil and also wood-tar oils, fuller's earth (a clay) has reduced color.

Decolorizing agents include "chars," which were made originally by charring bone; the residual carbon is accompanied by a calcium phosphate substructure. In using these decolorizing agents, they are added and suspended in the solution to be cleared of color; after some time, the suspension is filtered. For acid solutions, bone char is objectionable, as some phosphoric acid forms. The "vegetable chars" and specially trade-marked articles do not contain phosphates. One of them is carbon with 40 per cent fine sand which passes a 200 mesh sieve; the presence of the sand facilitates the suspension, and especially renders the subsequent filtration easy and rapid.

Plates for the filtration of very acid solutions, such as concentrated sulfuric acid, consisting of porous silica ware, have been received with favor (Filtros). A single plate is perhaps 10 by 10 inches; if a larger surface is desired, several plates are set in an acid-proof cement to form the roof of a box, to which suction may be applied to facilitate the filtration.

Shipping Containers

The mineral acids were shipped in former days in glass carboys of the balloon type, packed in hay or ground cork. For nitric acid, such packings are dangerous, and the Stahl carboy was developed, in which a 12-gallon bottle with straight sides is held in place by four strips of wood at the corners of the containing box; the surface of the strips (4 inches wide) is grooved to soften it. The dimensions of the box and of the bottle are so adjusted that the bottle can just be forced in place by gentle pressure. This style carboy was so successful that it has become standard for all acids.

Glass- and lead-lined containers were used exclusively for the shipment of sulfuric acid until steel tanks, portable and stationary, were introduced. This simplified the shipping of sulfuric acid and mixed acids, reducing the labor cost and the loss due to breakage; it took some

time to convince customers that acid shipped in steel drums holding 2000 pounds or steel tank cars holding twenty times as much was as good as acid shipped in the familiar glass carboys.[8]

Single tanks on a railroad flat car, used for many years only for crude oil and petroleum products, have gradually become standard in nearly all branches of chemical manufacturing. Steel for sulfuric acid and mixed acid is well known. Anhydrous ammonia is shipped in car tanks of similar size; single units for liquid sulfur dioxide, and for liquid chlorine, are in daily use. A tank of aluminum for 98 per cent acetic acid has been adopted as well suited. Steel tanks with a thin nickel lining have been introduced.[9]

Hydrochloric acid may be shipped in a steel tank car lined with wooden beams impregnated with ozokerite. Another suitable large-scale container is a rubber-lined wooden tank; usually 5 tanks are placed crosswise on a flat car.

Light sheet-steel drums with tight covers are much used, also steel barrels, tight wooden barrels for liquids, sometimes paraffin-lined. Square lead boxes in wooden protecting cases are used for hydrofluoric acid, also ceresine bottles. Mercury is transported in cast-iron flasks. Many solids are shipped in bulk, or in sugar barrels (not air-tight).

There is promise at the present time that a drum of light weight with welded joints will be developed, of chrome-iron alloy (17 per cent Cr), in which nitric acid made by the oxidation of direct synthetic ammonia, hence free from halogens, may be shipped. Tank cars of the same material suitable for such nitric acids are now constructed. Welded steel barrels or drums are being developed especially for the brewery trade.

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[8] Dr. Wm. H. Nichols said: "The first change from the carboys to iron or steel for sulfuric acid containers was a cylinder placed on a barge, capable of holding 50 tons of product. One small oil refiner was induced to put in a steel receiving tank, but for one whole year. a second one equally daring could not be found. It was feared not only that the acid would eat the container, and destroy it, but also that the acid itself would become weak." *Ind. Eng. Chem.*, 10, 768 (1918).

[9] Further details in "Regulations for the transportation by rail of explosives and other dangerous articles in freight, express, and baggage service, including specifications for shipping containers," Bureau of Explosives, 30 Vesey St., N. Y., Sept., 1930; and supplement # 5, to Jan. 20, 1933. Similar data may be found in the Condensed Chemical Dictionary, New York, Chemical Catalog Co., Inc., 1930.

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Chapter 46

Instruments of Control Used by the Chemical Engineer

Hydrometers

The concentration of a solution, for instance of sodium thiosulfate, is allowed to proceed until the density reaches a definite point, which trials have shown to be high enough so that on cooling a rich crop of crystals will be formed, yet low enough to contain enough water to form a mother liquor which will carry away the impurities; that density, in this case 51° Bé. for the hot liquor, is determined by means of a hydrometer. In countless other similar preparations of liquors, similar tests are made with the help of the same instrument.

In the manufacture of sulfuric acid by the chamber process, the amount of steam or sprayed water sent into a chamber depends upon the strength of the acid drips; this strength is determined by the hydrometer. For any process of dilution or of strengthening of this acid, and many others, the same instrument is used.

The simplicity of the apparatus needed insures its continued use; a container, usually a glass or lead cylinder, the hydrometer proper, and a thermometer, form a complete set.

Figure 246.—Hydrometer for liquids heavier than water, for the range in specific gravity of 1.500 to 2.00.
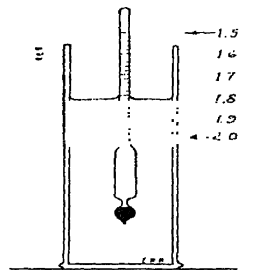
Hydrometers for Liquids Heavier than Water. A hydrometer is a float, with a lower wide chamber which is suitably loaded with mercury or iron shot, and an upper tubular chamber in which a scale is provided. The float is buoyed up to a height depending upon the specific gravity of the liquor; the higher the specific gravity, the higher is the float pushed up. The point on the scale on a level with the surface of the liquid, after the instrument has come to rest, is read. The construction of the hydrometer is shown in Figure 246.

The "common" hydrometer reads from 0° to 72° Bé., and frequently carries the equivalent metric values, the specific gravities, from 1.000 to 2.000. The smallest division is one whole degree, and can hardly be subdivided; this instrument is therefore used for the first approximation, indicating which one of the finer ones should be used next. A scale of ten degrees Baumé forms usually one instrument of the more accurate type, each degree being subdivided into tenths; these are wide enough to allow an estimate to within 0.02° Bé., equivalent to about 0.005 on the metric specific gravity scale. Hydrometers graduated for specific gravity readings are coming into use more and more; for the finer types, the scale covers one-tenth (thus 1.200 to 1.300), subdivided in ten hundredths, and each of these in ten thousandths; each of these last divisions may be subdivided by estimation into fifths, giving a final reading to within 0.0002 on the metric specific gravity scale. Thus for the space from 1.000 to 2.000 there would be ten glasses; such glasses are usually kept in the plant laboratory and the samples to be tested are brought there.

In order to insure accuracy to the last estimated place, a set of glasses [1] standardized at the Bureau of Standards in Washington is kept in the laboratory for comparison only; a second set, the one in use, is compared with the standards and the necessary corrections listed on the cover of the containing box.

Temperature Corrections. Such accurate hydrometers would have no meaning if at the same time the temperature were not determined; this is usually done by means of the same instruments, which carry an enclosed thermometer reading from — 10° to 40° C. or the corresponding values in the Fahrenheit scale. By means of tables, or in the absence of tables by means of determinations, a correction for temperature is applied, in order to reduce the readings to 60° F., the standard temperature.

For example, a sample of muriatic acid gave the reading of 21.6° Bé. at 74° F.; the correction for the range 22° to 25° Bé. is one-twenty-eighth degree Bé. to be added [2] for each degree Fahrenheit over 60°; hence

```
original reading ...................................  21.6
correction for error of scale  ....................    .0
correction for temperature 1/28 × 14 ..............    .5
                                                     ——————
                                                      22.1
```

As the acid must be 22° Bé., in this case, it just passes.
Using metric specific gravities the corresponding values would be:

```
original reading ...................................  1.1751
correction for error of scale  ....................        0
correction for temperature 0.00035 × 14 ...........    .0049
                                                     ————————
                                                      1.1800
```

[1] Such standard sets are usually the pride of the laboratory.
[2] For temperatures above 60° F. the correction is added; below 60° F., subtracted. 60° F. equals 15.56° C.

For control within the plant, the accuracy is not so great; a liberal margin of safety is provided by making the goods intended for shipment distinctly overstrength.

The relation between the Baumé scale and the metric specific gravity scale and a table for the Baumé scale for liquids heavier than water with the corresponding specific gravities is given in the Appendix.

Hydrometers for Liquids Lighter than Water. A water solution of ammonia decreases in specific gravity as its content of ammonia increases; the strength of the liquor is judged in this case also by means of a hydrometer which must be graduated in such a way that the further it sinks in the liquor, the higher will be the reading in degrees Baumé on the scale. This is therefore an entirely different Baumé scale, which is distinguished from the previous one by adding the words "for liquids lighter than water." The corresponding specific gravities

FIGURE 247.—Hydrometer for liquids lighter than water, for the range in specific gravity of 0.500 to 1.000.
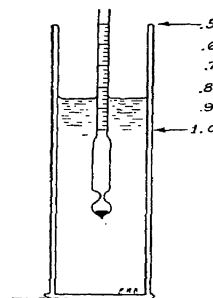
are less than unity. Such an instrument is shown in Figure 247. A table giving the Baumé scale for liquids lighter than water with the corresponding specific gravities will be found in the Appendix.

A correction for temperature differing for each liquid must be applied; for temperatures above 60° F., it is subtracted.

TEMPERATURE MEASUREMENTS

For temperatures between −20° C. (−4° F.) and 360° C. (680° F.), the ordinary mercury thermometer is used widely, in spite of the fragility of the glass container. Such an instrument is really a dilatometer; the expansion of the mercury at the various temperatures is measured against the glass scale. A nitrogen-filled mercury thermometer will read temperatures to 550° C. (1022° F.); such instruments are made of special, hard glass, which fuses only at still higher temperatures.

The application of the hand is also a practical method for judging moderate temperatures.

Thermocouples are used over practically all ranges of temperatures from that of liquid air (−190° C., −310° F.), to 1400° C. (2552° F.), which is the heat of a coal fire under forced draft. For temperatures between 500° C. (932° F.) and 1000° C. (1832° F.), resistance pyrom-

eters, especially platinum ones, are valuable. For temperatures above 1000° C., in addition to thermocouples, radiation pyrometers, optical pyrometers, and Seger cones are used in industrial plants. These instruments may each be used over wider limits than indicated. The choice of instrument will depend not only upon its special adaptability for the temperature range to be studied, but also upon the danger of deterioration if immersion in a fused chemical for instance is required; the radiation and optical pyrometers would then be preferred as they have the advantage of being operated at a distance from the furnace or hot object.

A single observation may be required once in a while, or regular observations at stated intervals, or constant readings; the latter are now made from charts marked by recording pyrometers, on which not only the high and low points appear, but the temperature at every moment.

Thermocouples. When two dissimilar metal wires are joined in two places and one junction is heated while the other one remains cold, an electromotive force is set up in the system which is a function of the temperature at the hot junction, provided the cold junction remains at an even temperature. (*See* Fig. 248.) Such pairs of wires are chosen
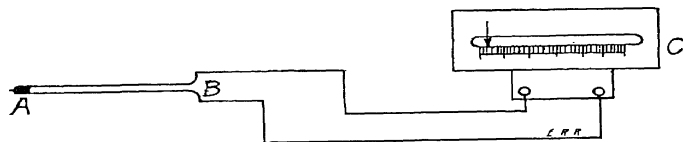
FIGURE 248.—Diagrammatic sketch of a thermocouple with millivoltmeter.

as will remain unaltered at the temperatures to be measured, and if several pairs are suitable, that pair is selected which gives the greatest increase in electromotive force for each degree rise; a third criterion, and not the least important, is the cost of the metals.

The electromotive force is measured on a millivoltmeter [3] which may be graduated in millivolts, or directly in degrees; if in millivolts, the degree corresponding to each reading is read off on a chart, on which the temperatures are entered as abscissæ, the millovolts as ordinates; for each thermocouple a separate chart is made by reading the electromotive force set up in two or more baths, or regions, of known temperatures; if graduated in degrees, a certain voltmeter must be used for a designated thermocouple, and the reading is direct.

The instrument in its simplest form is portable, and consists of the fire-end, which is the thermocouple proper, sheathed in an iron or porcelain protecting tube; two copper leads, and the millivoltmeter.

The electromotive force may also be measured by means of a portable potentiometer, in which the electromotive force set up in the thermocouple is matched by an oppositely directed electromotive force until a galvanometer needle shows zero current. Dry cells may be used for the matching current, and compared daily to a standard cell, such as the

[3] With high or low internal resistance; the high internal resistance type has the advantage that even considerable variation in the leads has no effect on the reading.

Weston. The potentiometer system for thermocouple currents is coming into increased favor; it is a little more complex than the millivoltmeter method, but no more than the platinum resistance pyrometer. It consists of the fire-end, the thermocouple proper, the copper leads, and the potentiometer box containing a cell, slide wire, and zero point galvanometer. The length of the drum-wound slide wire turned into the circuit is the measure of the matching current.

For precision work, in the laboratory, the cold junction which is here the binding post at the exit of the wires from the fire-end, is placed in an ice bath; in the plant, the temperature of the room is constant enough. The greater the difference in the temperatures of the two junctions, the less does it matter whether the room temperature is constant or varies somewhat; hence in this respect, high temperatures will be more accurately read.

The following pairs are suitable for the temperatures listed opposite them:

Copper—constantan	room temperature up to 500° C.
Silver—constantan	" " " " 700° C.
Iron—constantan	" " " " 1000° C.
Chromel—alumel	" " " " 1000° C.
Platinum—platinum + 10% rhodium alloy	" " " " 1400° C.
" " "	for short periods to 1500° C.

Constantan [4] contains 60 per cent copper and 40 per cent nickel; chromel, 90 per cent nickel and 10 per cent copper; alumel, 98 per cent nickel and 2 per cent copper. The alloy platinum-iridium is also used instead of platinum-rhodium.

The relative sensitivity is indicated by the figures in the table below:

	E.m.f. in Millivolts	
	at 500° C.	at 1500° C.
Copper—constantan	27.8	...
Silver—constantan	27.6	...
Iron—constantan	26.7	...
Chromel—alumel	20.8	...
Platinum—platinum + rhodium alloy	4.4	15.1

Resistance Pyrometer. The resistance of a coil of platinum varies with the temperature; this property is the principle of the resistance pyrometer. The coil is made one of the four arms of a Wheatstone bridge; a slide-wire, drum-wound, is adjusted so that the needle of a galvanometer shows no deflection; the length of wire needed for this adjustment is the measure of the temperature. The reading is direct, as the scale is graduated in degrees. The arrangement is shown in Figure 249.

The complete instrument consists of the fire-end, copper leads, a box containing a zero point galvanometer, a small dry battery, two resistances, and the slide wire wound on a drum forming itself the third resistance. The fire-end is usually an iron pipe closed at one end; at

[4] So named because its electrical resistance is practically constant over a wide range of temperatures.

its closed extremity, a small coil of platinum wire, wound on a mica frame in such a way that it can never touch the casing, is placed; the two ends of the wire are led out of the tube to binding posts at the open end; the wires are insulated from each other and from the casing by clay pipe-stem sections. The leads are long enough so that the box may be placed at a distance, on a convenient shelf against the wall.
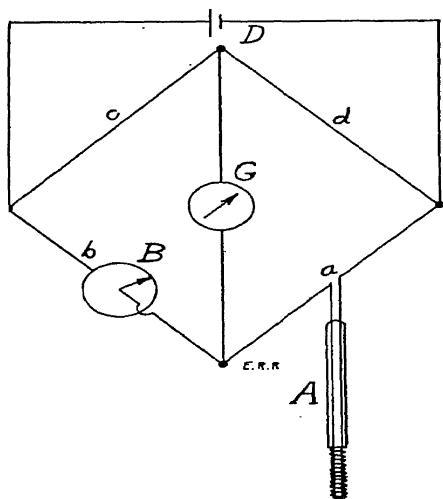
FIGURE 249.—The platinum resistance pyrometer. *A* is the fire-end, forming arm *a* of a Wheatstone bridge; *B* is the drum-wound slide-wire, forming arm *b*; *c* and *d* are the other two arms, which consist of fixed resistances; *G* is the zero galvanometer; *D* is the dry cell used for intermittent readings.

To make a reading a key is depressed to send a current through the system; at the same time the knob on the drum is turned until the galvanometer needle is at zero; the reading is directly in degrees.

In many cases the fire-end is fixed in the region to be measured and is not removed, although the whole instrument is portable. Readings are taken at stated intervals and entered on a sheet; correction of the fire is made at once.

The platinum resistance pyrometer is not as rugged as the thermocouple; it is also slower in response. If it is fixed in the region to be measured and not removed except for shutdowns; it is a reliable instrument and will give many years service. It is best suited for temperatures below 900° C.; for instance for the mechanical salt-cake furnaces, it has proved itself well adapted.

Radiation Pyrometer. The radiation pyrometer receives heat radiations from the furnace or hot body through a telescopic tube bearing at its farther end a concave mirror; just in front of the mirror and at its focus, a small thermocouple junction is located; the heat rays warm the junction, producing a current which is measured by means of a millivoltmeter graduated usually in degrees. The telescopic tube is set up on a tripod three feet from the door of the furnace for instance; by means of a finder integral with the tube, the latter is directed so that the heat rays will pass from the furnace bed along the tube to the mirror within; the

deflection is observed until it reaches a maximum which is the temperature sought. For comparative measurements, a line is painted on the floor, and the tripod is set exactly over this line for every reading; for absolute values, the instrument is calibrated by comparing it with a platinum resistance pyrometer in a small experimental furnace, gas or electric. With a door one foot square, the mirror must be within ten feet from the door; it may be as much nearer as convenient; the rule is that the distance must not exceed ten times the diameter of the object or region measured.

The radiation pyrometer is portable, and, like the other types, may be mounted in a fixed position; when portable, it consists of the telescopic tube, the tripod, the millivoltmeter, and copper leads. (*See* Fig. 250.)

The readings of the radiation pyrometer are reliable as absolute values only when a true "black body"[5] is observed; as this is rarely possible, errors due to partial absorption and imperfect radiation exist. For relative values at the same door of the same furnace, it is reliable. Furthermore it is our only means of estimating temperatures higher than the melting point of platinum.

FIGURE 250.—The radiation pyrometer. (Courtesy of the Brown Instrument Company, Philadelphia, Pa.)
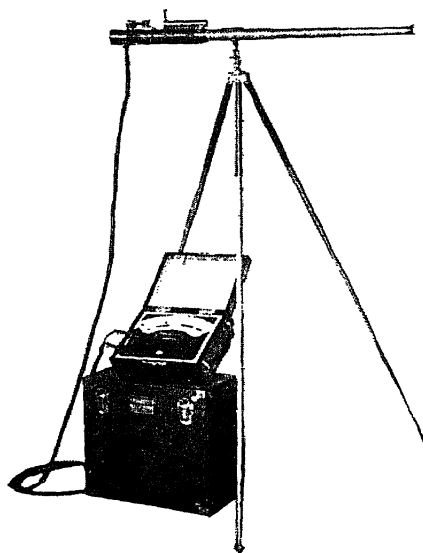
Optical Pyrometer.[6] The optical pyrometer shares with the radiation pyrometer the great advantage of not requiring introduction into the bath or region to be measured. The inner wall of a window-glass melting pot, for instance, is sighted through the instrument; in the field of vision a platinum loop is placed. The loop may be heated to dull red, bright

[5] A "black body" absorbs all incident radiations, transmits none, and itself radiates as fast as it absorbs.

[6] Optical pyrometers are radiation pyrometers limited to visible radiations.

red, or white, by sending a varying quantity of current from a dry cell through it. Just so much current is sent through as needed for exact matching of the field, when the wire loop cannot be seen at all; a little more current and the loop appears, and is whiter than the field; a little

Filament too dark.
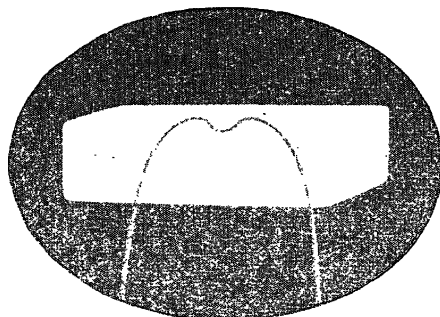
Filament too bright.
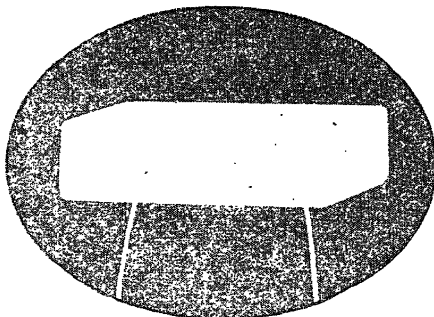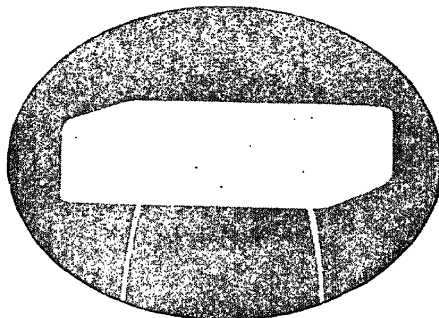
FIGURE 251. — Appearance of field when adjusting the current through the lamp filament to cause the latter to merge with the image of the hot object, in the optical pyrometer. (Courtesy of Leeds and Northrup Company, Philadelphia, Pa.)

Correct.

less and it appears again, but darker than the field. The reading for a perfect match is readily duplicated by different observers to within 4° C. near 1400° C.

The complete apparatus consists of the sighting tube containing the filament lamp, a storage battery, a rheostat, and a milliammeter. Its field of usefulness lies from temperatures corresponding to dull red, about 600° C., to temperatures higher than correspond to white heat.

Instruments procured from the dealers are ready for use, and are usually put into service without further testing. Should any doubt arise as to the correctness of the reading, the instrument may be sent to the Bureau of Standards at Washington, for certification. The standardization may be done in the laboratory of the plant if enough time is allowed to acquire the necessary technique, for it is specialized work, and very misleading figures may be obtained. The fixed points recommended are:

Melting point of Zinc			419° C.
" " " Aluminum			657
" " " Silver			961
" " " Gold			1063
" " " Nickel			1452
" " " Palladium			1549

The most reliable method of testing a thermocouple for the gold melting point for instance, would be to separate the wires at the fire-end junction (hot junction) and place a short piece of gold wire between them making good electrical contact; the rest of the apparatus would be as usual. On heating the fire-end slowly at a definite rate and watching the millivoltmeter, there will occur an interruption to the gradual rise of the needle and a sudden return to zero; the maximum reading made will correspond to the melting point of the gold. At least two such points are tested and the curve drawn for the intermediate temperatures.

FIGURE 252.—Pyrometric cones.
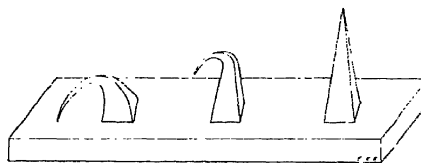
The comparison of two different pyrometers is another way to standardize; for instance, a radiation pyrometer may be sighted on the fire-end of a platinum-platinum rhodium thermocouple; or two thermocouples may be placed side by side. Sufficient time must be allowed for both instruments to reach their maximum reading, and the means of three trials is taken.

Pyrometric Cones. Pyrometric cones, formerly called Seger cones, are really slender triangular pyramids and are made of mixtures with definite fusion points. (*See* Fig. 252.) They are used in groups of three, numbered for instance 9, 10, and 11, set close together in a small lump of clay; the group is pushed into a porcelain kiln, as example, within range of a peep-hole. The firing will be increased until No. 9 melts and bends over completely, No. 10 softens enough to have its tip leaning over; No. 11 is still erect. If the firing is now maintained constant, or decreased, so that No. 11 remains unaffected, the maximum temperature which has been reached is that corresponding to No. 10, namely, 1305° C.; that corresponding to No. 9 has been exceeded, 1285° C., while that tempera-

ature corresponding to No. 11 has not been reached, 1325° C. It may be said that the temperature reached is determined to within 20° C.; this is not quite certain, but the observation of the cone may be made finer in this way: It is observed that the upper half of the cone leans over, the lower half is erect; that point is taken to be exactly 1305° C.; if only the upper third leans over, the temperature is about 1295° C.; if the lower half has started to lean over, the temperature is about 1315° C.; hence the accuracy may easily be said to be within 10° C. By making intermediate cones, the limit may be narrowed to 5° C. and less; the commercially obtained cones are made for 10° to 20° C. intervals, as that is close enough for ordinary operation in many industries. They are inexpensive, which is essential, as they are used but once.

For the range 1160° to 1810° C. Nos. 1 to 36 are made, leaving a difference of 10° to 20° between any two; the materials are feldspar, marble, quartz, and kaolin in varying proportions; No. 1 has 83 per cent feldspar, and only a trace of kaolin; whereas No. 36 has no feldspar, and all kaolin. The most widely used cones are Nos. 1 to 12, 1160° C. to 1335° C. Another series of ten numbers registers over a range of 895° C. to 1145° C.; and still another between 605° to 875° C. (Chapter 10).

Potteries are the plants in which Seger cones were chiefly in use; they still are, but of late the recording thermocouple pyrometer has been introduced. The cones will continue in use, however, where the accuracy of the temperature indication which they give is sufficient for the control of the operation. If a fluctuation of 20° C. does not matter, it is a waste of effort to make measurements within 4° C. The Seger cones suffer as all indicating instruments do, from the fact that they do not give information on how long a certain temperature was maintained; this is done only by the recording pyrometers.

Thermal Conductivity Cell for Gases. Supplementing chemical methods [7] for gas analysis, the thermal conductivity of gases has been made the basis of a method of analysis [8]; heat enters the gas through platinum spirals which receive a measured current. The heat conductivity values which follow will indicate the applicability of the cell:

Air	1.00	Ammonia	0.81
Hydrogen	7.35	Methanol gas	1.31
Carbon dioxide	0.58	Nitrogen	1.00
Sulfur dioxide	0.41	Oxygen	1.00

The cell for thermal analysis of carbon dioxide containing gases as manufactured by the Brown Instrument Company, may be taken as an example. Two gas wells are provided, through one of which (*O* in Figure 253), a portion of the gas to be analyzed is continuously bled, while the other (*P*) contains the comparison gas, air. In each cell there are 4 filaments (one is not shown in figure); each pair forms one arm of a Wheatstone bridge, hence two arms per cell, four arms for the two

[7] As to analysis of gases, read "New forms of gas analysis apparatus," G. A. Burrell, *Ind. Eng. Chem.*, **4**, 297 (1912). The simple Orsat apparatus is described in Chapter 12
[8] "Electrical gas analysis for continuous processing," A. C. Schmid, *Chem. Met. Eng.*, **36**, 230 (1929).

cells. A given current is passed through all filaments, heating them. Depending upon the thermal conductivity of the gas, heat leaks out to the metallic enclosing pipe, more or less fast. In the case of CO_2, it leaks out less fast than for air. As a result, the filaments in O are hotter,

FIGURE 253.—Cell for thermal-electric analysis of a gas containing carbon dioxide; see text. (Courtesy of the Brown Instrument Company, Philadelphia, Pa.)
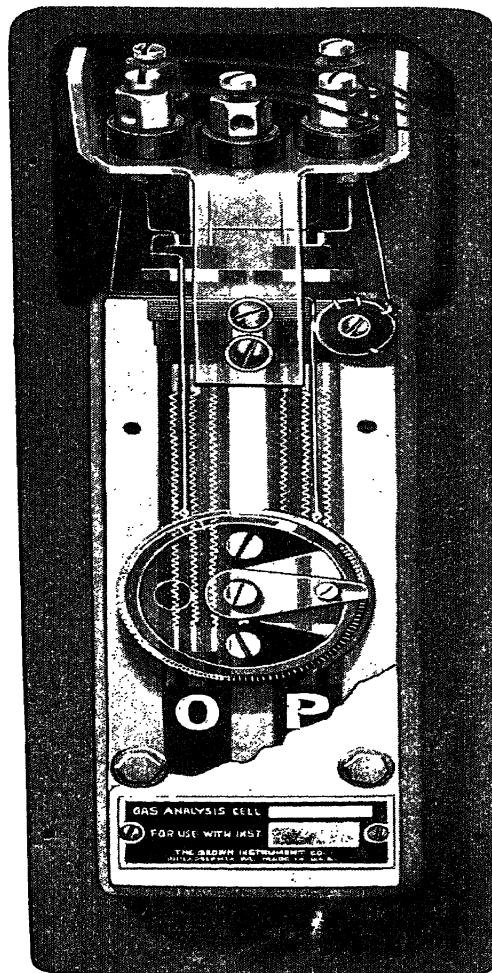
their resistance is greater; the bridge is unbalanced. A different current is then able to flow, and this actuates indicating and recording devices. A change in the composition of the gas is recorded in less than a minute.

In the *Ranarex analyser,* which depends upon the density of the gases for its action, there are two chambers, each with a driven impeller which drives the gas forward; and each with a fan wheel which receives the driven gas. Suitable outlets are provided for the gases. The impeller in

chamber A runs clockwise. The fan wheel tends to rotate in obedience to the impulse from the gas. It cannot rotate, however, because it is connected by an outside rod to the fan wheel in the lower chamber; here, the arrangement is the same, but the direction of the driven impeller is counter-clockwise; hence, the impulse on the wheel in chamber B is opposite to that in A. The same belt drives the two impellers. The rod which connects them registers the differential torque of the two fan wheels. If the gas in A is of the same density as that in B, the torque on wheel A will be equal and opposite the torque on wheel B, for the velocity given the gases are the same, and their densities do not differ. If the density of the gases differ, the torque differs, and there will be a movement of the rod toward one of them, away from the neutral position. This movement is magnified by means of levers and is transferred to a needle which travels over a scale.

The Ranarex was devised primarily for flue gas analyses; the density of carbon dioxide is very different from that of air (as 44 is to 28.8) and a small percentage, more or less, has an effect on the torque of the wheels, one running on air. For ammonia-air mixture, it has been equally successful; here again the difference in densities is considerable (as 17 is to 28.8). For ammonia, the chambers are kept dehydrated by sulfuric acid; for flue gas, they are kept hydrated by water.[8a]

Air Conditioning

In many industries, such as paper, textiles, printing, it is necessary to regulate the amount of moisture contained in the air of the factory rooms, for only by maintaining a certain humidity, at a given temperature, can the moisture-susceptible properties of the products be controlled. The "relative humidity" of the air is the ratio of water vapor actually contained in it to the maximum amount it may contain at that temperature. This latter would be saturated air, whose relative humidity would be 100. It is important that the temperature at which a particular relative humidity is to be provided, be stated, for the same relative humidity at different temperatures stands for different absolute amounts of moisture. Thus, 40 relative humidity at 65° F. corresponds to 36 grains of moisture per pound of dry air, but 40 relative humidity at 85° F. corresponds to 72 grains of moisture, per pound of air.

The relative humidity is determined by means of two thermometers tied together; one thermometer is left dry, the other is fitted with a wet cloth over its bulb. On placing these two thermometers, now termed a psychrometer, in the air to be tested, the wet bulb thermometer will register a lower temperature than the dry one. The differential will be greater the drier the air. From the temperatures, the relative humidity is read off on the chart (*see* Fig. 254), and applies to air at the temperature of the dry bulb thermometer. The absolute amount of moisture in grains, per pound of dry air, may also be found by means of the chart.

With a sling psychrometer, the necessary equilibrium is attained in a minute.

Air conditioning means providing air with a definite, predetermined amount of water vapor, at a stated temperature. Partial humidification means the injection of atomized air in the rooms, in order to raise the moisture content. Complete humidification means either lowering, or raising of the moisture content, as may be necessary. For the latter,
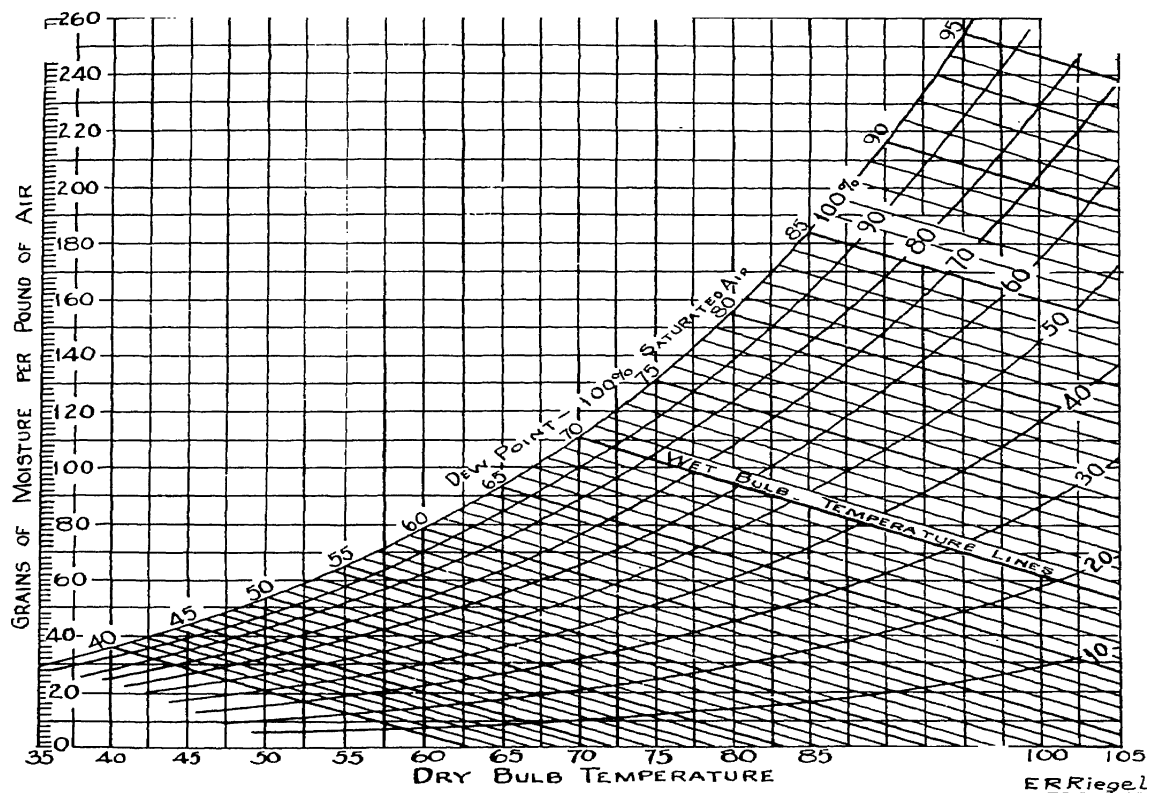
FIGURE 254.—Psychrometric chart, for determining the absolute and relative humidity in the air from wet and dry bulb thermometer readings. The curved lines are the relative humidities.

as a rule, outside air is passed through a spray of circulated (and cooled) water at a low temperature; the air becomes saturated with moisture at the temperature of the spray. This may involve a cooling, and a deposition of water (dehumidification). Next the air passes baffles in order to deposit entrained droplets, and finally over steam coils in order to raise it to the temperature prescribed. There are many variations in procedure. In all, a fan pulls in the new air, and delivers it to the ducts

leading to the various rooms.   Refrigeration and silica gel have been used for dehumidification.

The Cottrell electrical precipitator (described in chapter 43) has been applied to air conditioning. Its special efficacy is the removal of suspended solid particles below 5 microns in diameter, which are frequently of bacterial nature, and which escape the ordinary dry filter. The Westinghouse Electric and Manufacturing Company is about to announce (March 1937) a commercial Cottrell unit suitable for the home. The unit will follow the dry filter. The charged particles will pass between plates with a voltage gradient of about 1400 volts per inch. All danger of ozone or nitric oxide formation is avoided by lowering the voltage to 15,000 from the original 60,000.

MEASUREMENT OF THE FLOW OF GASES

The measurement of the flow of a gas is a frequent operation; the quantity of a waste gas, sent up a chimney for instance, may be sought because of a certain content of a valuable gas or vapor; if the volume of gas passing out is known, an analysis giving the percentage by volume of the valuable gas is all that is needed to make the calculation as to how much is lost per day.
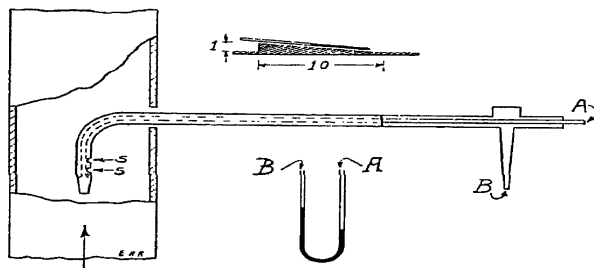
FIGURE 255.—A brass Pitot tube. *A* and *B* are connected to a vertical *U*-tube as indicated; for low velocities, the inclined manometer shown here is used.

The Pitot tube and the Venturi tube both measure velocity per second, and this multiplied by the area of the pipe gives cubic feet per second. An occasional measurement for which no installation has been provided is made by means of the Pitot tube; the Venturi tube is built into the line, and all the gas passes through it at all times.

Gas flow meters for small rates of flow may be constructed in the laboratory, and of glass.[9]

The Pitot Tube. The Pitot tube is a double tube, as indicated in Figure 255. One opening, facing upstream, receives velocity head and static head [10] combined; a rubber tube transfers this double pressure to one leg of a *U*-tube. Two small pin-hole openings permit the static pressure to pass through the outer chamber through a rubber connection

[9] *Ind. Chem. Eng.*, **11**, 623 (1919).
[10] The static head is the absolute pressure in the pipe.

to the other leg of the U-tube; in this way, the static pressure is eliminated in the reading; the difference in levels in the two legs of the U-tube is due to velocity pressure alone. The U-tube is filled with ether, or thin oil, or some other chosen liquid; for low velocities, the lightest liquid is used, ether, in order to obtain as large a reading as possible. The accuracy of the reading is increased by ten by inclining the U-tube to near horizontal position, on slope of 10 to 1; this form is known as the Swan manometer. With the height expressed in terms of a vertical column of water, the formula $v = \sqrt{2gh}$ is used, usually with a factor of 0.9 to allow for the dragging effect of the pipe walls.

Venturi Tube. If the normal diameter of a pipe be narrowed to form a throat, then flared out again to the original size, another means is provided to measure velocity. The relation between the diameters and the length of the constricted portions is approximately as indicated in Figure 256. The pressure at the throat will be lower than in the
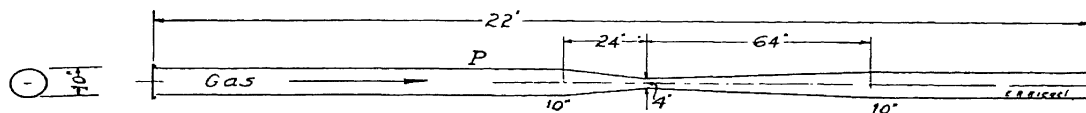
FIGURE 256.—The Venturi tube for measuring the flow of gases; a small pipe is soldered to the 4-inch throat, another at *P*, and connected to a U-tube.

full-sized pipe, if a gas is traveling through, and the difference between the two pressures, measured on a U-tube as before, is proportional to the velocity. In chemical plants, it is customary to standardize each Venturi tube by sending known volumes of air at various temperatures through it, and recording the readings. The theory is essentially the same as for the Pitot tube.

The Venturi tube may be vertical or horizontal, of lead or cast iron; the liquid in the U-tube is usually water, sometimes concentrated sulfuric acid, rarely mercury.

In the Thomas meter, essentially an electrical thermometer, a measured quantity of heat is furnished a traveling gas at a given point in the conduit; the increase in the temperature of the gas is inversely proportional to the quantity passing through per second; the more gas passes, the smaller the rise in temperature. A modern form of this valuable device is illustrated in Chapter 14.

In an orifice flow meter (*see* Fig. 257), a disk is inserted in a pipe which stops the flow of the gas except for a small circular opening at its center. This impediment in the path of the flowing gas causes a difference in the pressure, which is higher just before it, and lower just behind. The pressure difference may be read hydrostatically, or a more elaborate device may record the changes in pressure, hence the flow, by various means. In the Brown Electric Flow Meter, the pressure acts on a reservoir of mercury, causing more or less mercury to pass to the

float chamber, which in turn causes a stainless steel float carrying a magnetic armature on a non-metallic nickel-chromium rod to move up and down. The steam and float are enclosed in a non-magnetic ferrous alloy tube. Over the outside of this tube a divided inductance coil fits. Auxiliary electrical apparatus passes more or less current, as the divided inductance coil is affected more or less by the magnetic armature within the closed tube. The auxiliary apparatus includes indicating and recording devices.
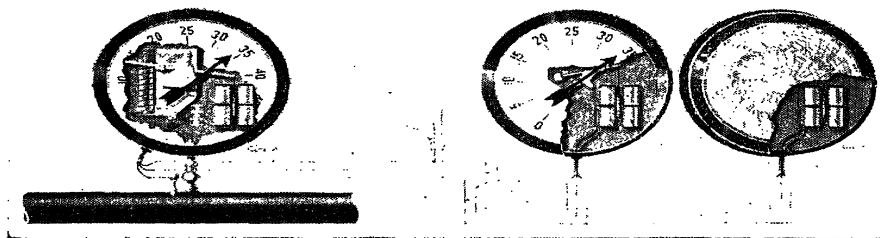
FIGURE 257.—An orifice electric flow meter, indicating and recording. (Courtesy of the Brown Instrument Company, Philadelphia, Pa.)

The Rotameter is a flow meter for liquids. It consists essentially of a tapered tube flaring upward, through which the liquid travels in an upward direction. A top-shaped rotor is placed in the tube, which may be Pyrex Glass, and is held in suspension by the upward flow of the liquid. The faster the flow, the higher must the rotor be carried, in order to allow the flow past its circumference. The height is read on a millimeter scale, and is standardized for volume flow.

ELECTROMETRIC METHODS IN PLANT OPERATION

In a number of industries, the control of the acidity, or in more general terms, of the concentration of hydrogen ions, is of great importance for uniform production. A number of devices for the electrometric determination of this value have been successfully introduced.[11] The development of such methods for laboratory use, that is; chiefly analysis,[12] had to precede, and this has been in progress for the last fifteen years or so. Two main divisions may be observed.

The first is a conductivity group, in which a measurement depends upon the conductivity of a solution to the electrical current, whether that conductivity be due to activity, alkalinity, or to salts. If it is known that salts are absent, and that only one certain acid can be the cause of the conductivity, this method can be used for the control of acidity.

[11] "Progress of electrometric control methods in industry," Henry C. Parker, *Ind. Eng. Chem.*, **19**, 660 (1927).

[12] Consult "The determination of hydrogen ions," Wm. M. Clark, published 1928 by Williams and Wilkins Co., Baltimore; also the chapter on "Electrometric methods in analytical chemistry," by N. H. Furman, pages 823-863 in Vol. 2 of "Treatise on physical chemistry," H. S. Taylor, New York, D. Van Nostrand Co., 1925.

The second group is the potentiometric group, applied chiefly to the determination of hydrogen-ion concentration in a solution. Its superiority over any other method lies in the fact that it is applicable even in the presence of salts, and to colored solutions which would prevent the use of indicators. The method rests upon the measurement of the potential of a primary [13] cell made up of two halves, one the hydrogen half, the other the calomel half, a saturated solution of calomel in contact with a potassium chloride solution. Such a cell generates a small current of a definite potential (voltage) if the solution in which the hydrogen electrode rests is normal. The calomel half-cell remains constant. By hydrogen electrode is meant a platinized platinum rod or plate over which bubbles of hydrogen pass at the rate of three a second, or similar rates. If the concentration of the acid solution is varied, the potential of this composite cell will also vary, and the variation will be directly proportional to the change in concentration. Hence this provides a means of following changes in the concentration of the hydrogen ions; with the addition of electrically controlled mechanisms, correcting solutions may automatically be introduced. The potential is measured by matching it with a second potential in the opposite direction from an outside source, lowered or raised by the introduction or removal of resistance, until a galvanometer between the two circuits indicates no flow. The amount of the resistance introduced or removed is the real measure of the potential change.

The industrial cell may employ the hydrogen electrode, or this may be replaced by the tungsten or pyrolusite electrode or other non-gas electrodes. A rugged cell entirely protected by a Bakelite sleeve, with all the necessary apparatus transportable, is described in the literature.[14]

The electrometric methods of the first class, depending on conductivity, and measured and applied to control by means of a Wheatstone bridge with auxiliary apparatus, serve to detect leakage in surface condensers in power plants. The condensed water is pure and does not conduct the current, but if any cooling water enters through a newly developed hole, let us say it is sea water, the contaminated condensed water will at once allow the current to pass; by means of auxiliary mechanism, a red light will appear announcing the leak.

Control by means of the measurement of the potential due to hydrogen-ion concentration has been applied to the automatic addition of caustic soda and sodium phosphate to boiler feed water which is acid, to maintain the proper acidity in a neutralizing bath for alkali cotton, and to several other industrial problems.[15] Temperature must always be taken into consideration.

A recent development for the rapid determination of carbon in a molten steel while it is in the furnace, open hearth or electric, is the *Carbometer*,[15a]

[13] That is, "current-producing cell," in distinction from the electrolytic or "current-consuming cell."
[14] *Ind. Eng. Chem.*, **17**, 639 and **737** (1925).
[15] *Ind. Eng. Chem.*, **19**, 660 (1927).
[15a] Carbometer, patent of Malmberg-Holström, manufactured by Aktiebolaget Alpha, Sundbykerg (near Stockholm), Sweden.

a Swedish instrument which utilizes the degree of magnetic induction which can be imparted to a test sample of steel; the magnetic induction varies with the carbon content. A $\frac{3}{8}$-inch rod is cast from the spoon sample, quenched, and placed in one of two funnel-shaped vertical receivers in the carbometer; one slot is for hardened steel (over 0.40 per cent C.), the other for unhardened steel. Turning a knob starts the clockwork which drives an armature; the test piece is magnetized. When the armature stops rotating (clicks), pressing a button allows the final rotation of the armature from the highest magnetic field strength position, through 90°, to the lower field strength, inducing a current of electricity in the coil surrounding the test sample. This current is measured on a ballistic galvanometer, shunted in automatically when the armature reaches its final position. The needle reading is translated into carbon percentages by means of a chart, read to within 1 point (0.01 per cent C.). Charts are made at the plant for the types of steel manufactured, inasmuch as other metals alter the magnetic induction. The readings are checked against laboratory analyses.

The refractometer is a useful instrument of control. For example, in the process of hardening vegetable and animal oils to fats, the progress of the hydrogenation may be followed by the change in refractive index. A few drops on the split prism of an Abbé refractometer, with water circulation to give a definite temperature, permit a reading in a few seconds.

An automatic sampling device, for sampling wood chips, or any material from a spout, to a conveyor, for example, has been described.[16]

Unit Operation. In 1915, Dr. Arthur D. Little observed that "any chemical process may be resolved into a co-ordinate series of unit operations, as pulverizing, drying, roasting, crystallizing, filtering, evaporation, electrolyzing, and others." This suggestion has become part of the system of chemical engineering study.[17] Other unit operations are agitation and mixing, fractional distillation. The process of making caustic soda by causticizing soda ash with lime is divided into four unit operations: lime slaking, causticizing, caustic liquor decantation, lime mud washing.

OTHER PATENTS

U. S. Patent 2.020,588, fluid flowmeter; 2,021,615, liquid level indicator; 2,012,616, method and apparatus for introducing reagents into liquid suspensions; 2,022,695, controlling flow of volumes of liquids; on pyrometers and thermocouples, 1,890,701; 1,808,507; 1,820,219, optical; 1,825,229, and 1,788,849, same; 1,845,271, thermocouple; 1,849,832, thermocouple for high temperatures, with a carbon and a tungsten element; 1,823,706, same, but tantalum carbide and graphite elements.

PROBLEMS

1. The outside air is 40° F. and 30 relative humidity. This air is moved into the building, gradually warming to 76° F., with no gain or loss of heat. What is the relative humidity for such air in the building, and what would the psychrometer readings be?

[16] *Chem. Met. Eng.*, **37**, 350 (1930).

[17] "Unit processes and principles of chemical engineering," J. C. Olsen, New York, D. Van Nostrand Co., 1932. *See also* final reference under "Reading References."

Answer: 9 relative humidity; 76° F. dry bulb; 49° F. wet bulb.

2. Starting with any air, how would you furnish a room with air at 72° F. and 50 relative humidity?

Answer: Cool or warm to 51.5° F. and saturate with H_2O at that temperature, then warm to 72° F.

3. A sling psychrometer gives readings: wet bulb, 60° F.; dry bulb, 78° F. What is the relative humidity? This air is completely dessicated and then warmed to 78° F. again. What is its relative humidity, and what are the wet and dry bulb readings?

4. For a comparison of heat effects, the following purely theoretical comparison should be made: Air at 80° F. and relative humidity 80, at the rate of 10,000 cu. ft. per minute, passes over a water surface; it takes up more moisture until saturated. How much water in pounds per pound of air are taken up, and how many Btu. does their vaporization represent?

To cool this air to 55° F. means the removal of how many Btu., equivalent to the vaporization of how many pounds of water? If the heat consumed in the vaporization in the first part of the problem is not sufficient, how many pounds of water at 55° F. will be required to remove the remaining Btu. by contact, without vapor exchange?

Take the mean specific heat of the air as is over the range specified as being 0.01826 Btu. per cu. ft., and the heat of vaporization for 1 pound of water over the same range as 1060 Btu.; take 1 cu. ft. of the air as is to weigh 0.0761 pound.

5. In reality, when 80° F. air with 80 relative humidity is cooled slightly, the temperature will drop to wet bulb temperature, the loss of sensible heat being equal to the gain in latent heat of water vaporized. The latent heat is the heat obtainable when water as gas becomes liquid water. What is the wet bulb temperature which goes with our original datum?

A pound of air at a dry-bulb temperature of 80° F. and a wet-bulb temperature of 75° F. contains 124 grains of water. When such air passes through a spray of water at the same temperature, water will be taken up. The dry-bulb temperature will fall, but the wet-bulb temperature will remain 75° F., and the dry-bulb temperature will equal it. The dew point, which is originally 73° F., will gradually rise to 75° F., when saturation is realized. How many grains of water will it contain now, and what is the gain?

At ordinary temperature, 1 grain of water absorbed means a lowering of about 8.5° F. in the dry-bulb temperature.

6. An air-conditioned system delivers to the space to be conditioned 20,000 cu. ft. of air per minute at 65° F. dry bulb and 40 per cent relative humidity. Of this air, 75 per cent is being recirculated. Determine the refrigeration effect, in tons, required when the outside air has 90° F. dry bulb, and 77° F. wet bulb, the return air has 75° F. wet bulb, and relative humidity of 34 per cent, and the total 20,000 cu. ft. passes through a saturating air washer. Assume 13.6 cu. ft. of air per pound.

Note: The standard refrigeration ton is 200 Btu./minute, or 12,000 Btu./hour or 288,000 Btu./ day. The value per day is the one generally used. A complete psychrometric chart may be obtained from any firm which manufactures blowers or air conditioning equipment. For example, address the Buffalo Forge Company, Buffalo, N. Y.

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"Absorption and Extraction," Thomas K. Sherwood, New York, McGraw-Hill Book Co., 1937.

"New carbometer control speeds production and improves quality," Gilbert Soler, *Metal Progress,* **31,** 159 (1937).

"Automatic detection and control of hydrogen sulfide," S. Roberts and G. Minors, *J. Soc. Chem. Ind.,* **53,** 526 (1934).

A proposed complete list of unit operations and unit processes will be found in the collection of "Flow Sheets of Process Industries," published as a separate loose leaf book by "Chem. and Met.," McGraw-Hill Book Company. 1934. The flow sheets will also be found in the regular issues of *Chem. Met. Eng.* The first collection is supplemented by an additional one on more recently developed processes; these also will be found in the regular issues of the same magazine, for the year 1935.

Of the long list of metallurgical products, pig iron and steel exceed in production many times that of any other metal. Some of the newer products have received much advertising, necessary because of their newness, but tending to produce a wrong conception of their relative importance. Pig iron and steel are the giants, now more than formerly. Pig iron production figures are commonly taken as an index of the general prosperity of a country. It is a basic industry, serving many others.

Chapter 47

Pig Iron *

The manufacture of pig iron is on an enormous scale, as the figures in Table 75 will indicate.

TABLE 75.—*World Production of Pig Iron.*

	1929	Gross Tons 1932	1935
United States	42,614,000	8,781,453	21,373,699
England	7,580,000	3,573,000	6,426,400
Germany	13,401,000	3,932,026	12,342,415
France	10,439,000	5,537,000	5,799,000
World total	96,263,000	26,578,409	51,070,343

The pig iron production (U. S.) has fluctuated widely in the past years; a high of 42,286 thousand long tons, in 1929, became a low of 8,686 thousand long tons in 1932, since when the production has climbed steadily to 30,618 thousand long tons in 1936.

The process in brief consists of heating an iron ore, an oxide, with coke in an upright furnace having continuous operation; hot air under pressure is pumped into the furnace at the base, and by causing the coke to burn, produces a high temperature. The iron oxide is reduced to the metal which collects at the lowest spot, and is tapped off at intervals; the hot fluid iron unavoidably dissolves some carbon (3 per cent). The solids added at the top are iron ore, coke, and limestone; the latter binds much of the silica present as impurity in the ore, and forms with it and other substances the slag, which also flows to the bottom of the furnace. The liquid slag is lighter than the liquid iron and floats on it; it is tapped at frequent intervals through a special tap hole, further up than the iron tap hole. In nearly all cases, a mixture of several kinds of ores is preferred to a single one.

The oxide richest in iron is magnetite, Fe_3O_4, with 72.5 per cent Fe; it is found very pure in Sweden and in a few places along Lake Superior.[1] The next oxide, Fe_2O_3, nearly as rich in iron (70 per cent Fe when absolutely pure), is the most important one. It is the chief ore of the Minnesota deposits.

* Based on studies of a Buffalo furnace, made with the assistance of Dr. Kenneth McAlpine, of Princeton University.

[1] Magnetite deposits occur also in New York, Penna, New Jersey, New Mexico.

Iron ore mined in United States in 1935 amounted to 30,540,252 gross tons, at 144 mines in 16 states; its value was close to 80 million dollars. In Minnesota, 19.37 million tons were produced, in Michigan 5.2, in Alabama 3.27, in Pennsylvania, 1.0, the rest in smaller states' totals.

As an example of American practice, the Fayal mine in northern Minnesota, about 60 miles from the lake shore (Two Harbors), and part of the Mesabi range deposit, will be briefly described.

The Fayal mine is an open pit mine; the removal of about 20 feet of overburden discloses a vast body of red ore, most of it soft enough to work with a steam shovel. Various levels are worked, as the quality differs slightly; movable railroad tracks are laid on inclines. The empty ore cars are pulled to the desired spot, where a steam shovel (or several) awaits them; the cars are loaded in a short time, without hand labor. A powerful locomotive pulls the cars up the incline and starts toward the lake port, Two Harbors. The train passes at a slow rate over scales, and the weight is read and recorded as the train moves. By the time it reaches Two Harbors, the chemical analysis of the loaded ore is finished and its exact grade determined; this permits a train dispatcher to send the cars to certain pockets in a certain dock, there to be dumped with similar ore. The cars are dumped by pulling the level which opens the bottom. The ore boats are loaded in a simple but rapid way. The ore pockets in the docks are elevated, so that by lowering a chute and drawing a gate, the ore is served to the boat by gravity. On approaching, the lake boat whistles its requirements as to quality; a siren at the end of the central dock screeches back signals which tell the boat at which dock, and in front of which pockets in the dock, it should anchor. The boat pulls in with its hatches open, and while still being anchored, the chutes are lowered and the ore rumbles into the boat. In thirty-nine minutes, it can be on its way out with a load of 11,000 tons, (record in 1909).

TABLE 76.—*Actual Reserves of Iron Ore in the World (1926).*[*]
(*Major Deposits Only*)

	In thousands of tons
United States	10,452,225
France	8,164,350
Brazil	7,000,000
Great Britain	5,969,600
India	3,326,110
Cuba	3,159,000
Sweden	2,203,350
U. S. S. R.	2,056,850
Spain	1,115,500
Union of South Africa	1,095,135
Total, World	57,811,923

[*] "World iron ore reserves now exceed 57 billion tons," O. R. Kuhn, *Eng. Mining J.*, (July 17, 1926).

An extensive deposit of hematite containing generally some phosphorus stretches from New York State to Alabama, and is mined in several of the States it traverses.

In order to manufacture pig iron, coke is required as well as ore; in the order of tonnage of pig iron produced, the States are Pennsylvania, Ohio, Illinois, Indiana, Alabama. It will be noticed that the centers of production are those which have coal and coke, rather than ore, and it is a general rule that "ore follows the fuel." It is easier to transport the ore, without damaging it, than the bulky coke, which crumbles on handling; the primary production district since coke has displaced charcoal and anthracite is Pittsburgh, where the Connellsville beehive coke is available. The Minnesota ore was transferred to railroad cars at near-by lake ports for the short haul to the Pittsburgh and Youngstown districts. Of late years, more and more plants have been located at the lake ports, so that the ore boat might unload directly in the yard of the blast furnace plant (Buffalo, Cleveland, Detroit, Gary, Chicago). In Alabama (at Birmingham and other places) the ore and the coal are both found in the district, and in addition, suitable limestone beds; the pig iron made there is therefore very low in cost. A less important center is Colorado. Still another agency is at work decentralizing the pig iron industry, namely the by-product coke oven, which has surplus coke suitable for iron-making for sale at low prices. Along the Atlantic seaboard (Baltimore, Philadelphia) ore from Cuba, even from Sweden, Elba, Spain, and Chile, may be imported at reasonable cost, and with the aid of by-product coke, pig iron manufactured.[2]

In England, very pure ores free from phosphorus are mined; with the rich coal resources of Great Britain, the iron industry has long flourished. France has in the Lorraine deposits a large tonnage of low-grade (30 per cent Fe) ore which contains phosphorus, but also calcium carbonate, so that by skillful working a phosphorus-containing pig iron, suitable for the basic Bessemer process for steel, can be made. The deposit is 30 miles long and 12 miles wide, and in its eastern part is mined at the surface. The greater part of the pig iron and steel production of France and Germany comes from this Lorraine ore.[3] In Sweden, very pure iron is made with charcoal, from native ores; this pure product is still the basis of the cutlery manufacture of Sheffield. In southern Russia, iron is produced in considerable quantities. China has rich ore deposits, while her coal resources are second only to those of the United States; in the future, it is probable that the present plants (Hankow) will be extended and others erected.

Several representative analyses [4] of iron ores are given in Table 77; much of the Minnesota ore is low enough in phosphorus so that the pig iron made from it may be converted into steel in the acid Bessemer

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[2] Bethlehem, Pa., is not too far from seaboard to use foreign ores, mixed with western Pennsylvania ores.

[3] A portion of the deposit lay in the part of Lorraine held by the German empire during 1871 to 1918; its importance was unknown in 1871, for it was only after the English improvement of the Bessemer process, the Thomas-Gilchrist basic lining, that the Lorraine ore could be made into good steel; the effect is plain from the German production figures for steel: 1880, one-half million tons; 1913, 18 million tons. The following figures will indicate the quality of the ore for the Lorraine district, more particularly for the Landres basin, one of the 4 main divisions: Fe 40%, CaO 10%, SiO_2 6%, Al_2O_3 7%, P 0.65%.

[4] Cargo analyses for the season 1925, The M. A. Hanna Co., Buffalo and Cleveland.

Table 77.—*Mesabi Range (Minnesota).*

	Suitable for Acid Bessemer Per Cent	Special Very Low Phosphorus Per Cent	Manganiferous Per Cent	High Phosphorus Called "Non-Bessemer" Per Cent
Iron, Fe	60.72	63.12	53.23	61.37
Phosphorus, P	.039	.017	.036	.083
Silica, SiO_2	8.43	7.45	9.37	3.94
Manganese, Mn	.22	.09	4.77	.38
Alumina, Al_2O_3	.54	.46	.72	1.60
Lime, CaO	.25	.05	.31	.15
Magnesia, MgO	.14	.09	.13	.13
Sulfur, S	.006	.007	.007	.011
Ignition loss (H_2O)	3.91	.95	6.68	5.88
Name of ore	LaRue	Patrick	Sliver	Beaver

converter; other shipments have enough phosphorus to produce a pig which must be handled in the basic open-hearth steel furnace. All analyses are on samples dried at 212° F., hence free from moisture.

The ores from other ranges in the Minnesota-Michigan deposits are similar to the four shown in the table, and indicate the same wide variety. The price depends upon the iron and the phosphorus content. If the La Rue ore sells for $5.00 (or $4.00), the Beaver may be $3.50 (or $2.50); this is the usual range of normal prices. The general average for all ores in 1935 was $2.48; in 1934, $2.58.

The Blast Furnace

The blast furnace consists of a steel shell circular in cross-section, lined with hard fire-brick; the shell stands upright; the upper two-thirds or so flare out downward, while the lower third flares in. The purpose of the upper flare is to permit the charge to slide down readily and fill any holes which might develop; with straight sides, it often happened that large cavities formed, so that after a while a sudden descent (a slip) took place, which at times proved disastrous. The lower flare in the opposite sense is required by the removal of the coke by combustion, and the running down of the melted iron, causing a great contraction. The bottom of the furnace is the hearth, where the liquid iron, overlaid by the liquid slag, collects. The charge in the furnace is called the "burden," and is introduced at the top through a vestibule-like arrangement which prevents the escape of gases; the materials fall first onto an upper bell, which is depressed in order to allow the materials to drop into an intermediate chamber whose floor is formed by a second bell. When the second bell is depressed, the charge enters the furnace; at such times, the upper bell is shut tight. This bell is also rotated, so that the charge is placed evenly over the surface of the furnace content. The liquid iron and the liquid slag are removed periodically by tapping; the slag hole is formed by a water-cooled metal piece, situated above the iron hole; through the latter, the iron is allowed to find its way out. The taphole for iron is in brickwork. At the end of the tapping, the iron hole is closed by a plug of clay, applied by the "mud

gun," with a fast-moving piston which forces the clay into the hole. The slag hole is easily closed by an iron plug on a long rod (the slag hole is only about 1¾ inches in diameter.)

The air blast for the combustion of the coke enters through the bustle pipe, a steel pipe 3 feet in diameter lined with fire-bricks, because the air is applied very hot (average 1600° F.). The blast passes from the
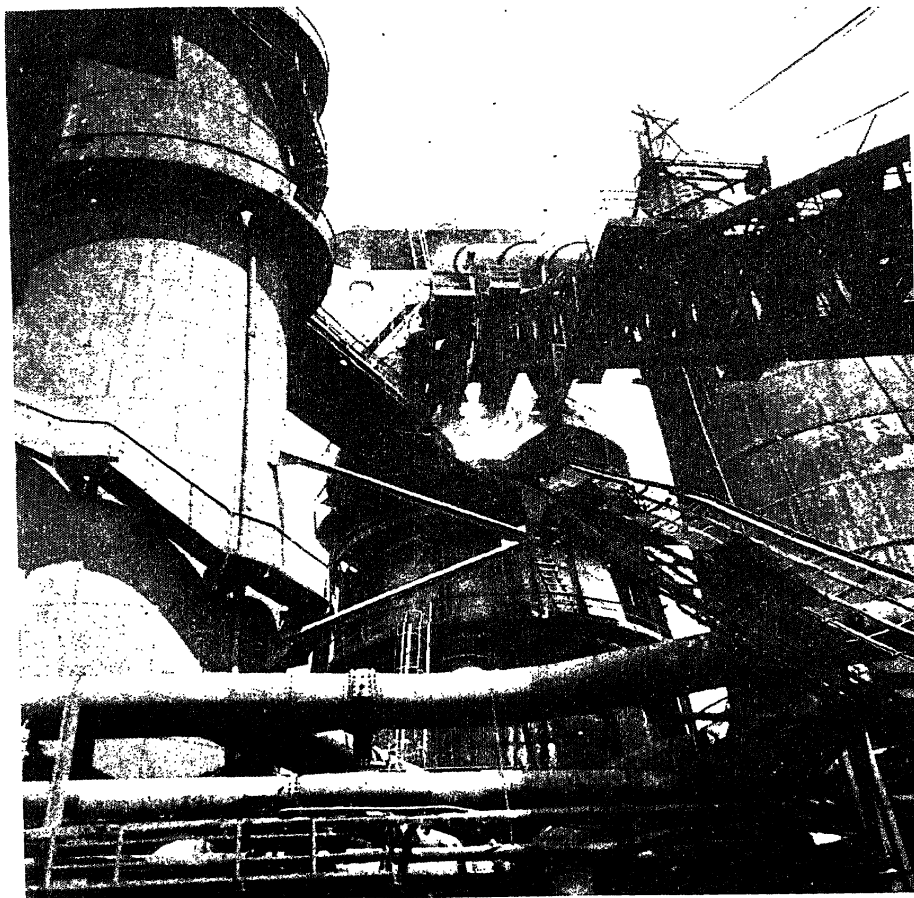
FIGURE 258.—Iron blast furnace and stoves, the Petrovsky plant at Dnepropetrovsk, Ukraine, U. S. S. R. (By permission.)

bustle pipe to the furnace through the tuyeres, which are partly lined and partly water-cooled. Each tuyere has a sight hole and may be cleared by a rod if anything blocks it from the inside.

The hottest part of the furnace is the lower part, where the tuyeres serve the blast; the constricted part just above the tuyeres, the portion of the furnace which flares in (downward) and which is called the "bosh," receives the blast first and furnishes intense combustion.

The weight of the upper part of the furnace is carried by a number of columns (12 to 18) resting on an elaborate foundation on which the bosh also rests.

In order to present a definite example of blast furnace practice, a furnace 92 feet high and 23 feet wide at the widest (inside) diameter will be described; such a furnace is represented in Figure 259, showing the complete furnace with the skip hoist which lifts the charge to the
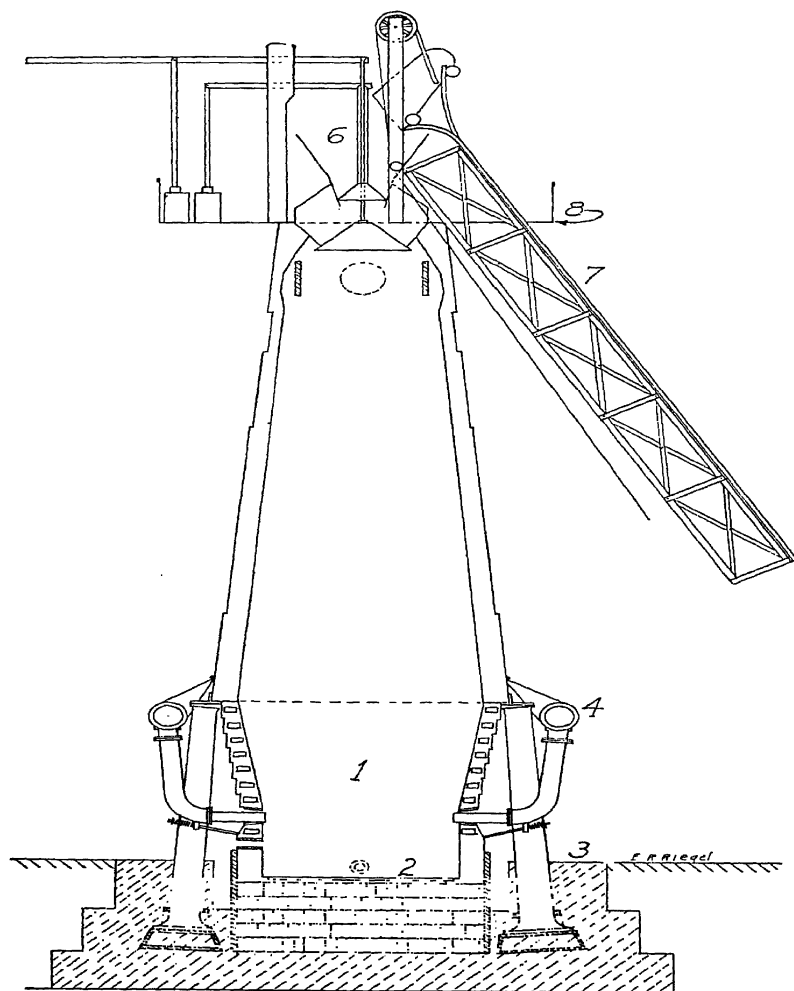
FIGURE 259. — The blast furnace for iron, showing the furnace proper, with 1, the bosh; 2, the hearth; 3, the foundation; 4, the bustle pipe and tuyeres; 6, the double bell for introducing the charge; 7, the skip hoist; 8, platform at top of furnace. The dotted circle under the bell is the outlet for the gases. The distance from 8 to the hearth line at 2 is 92 feet.

furnace top. In a second sketch (Fig. 260), a closer view of the bustle pipe, tuyeres, slag hole, and bosh wall is given; it will be noted that the bosh wall carries metal boxes which are water-cooled, thus lowering the temperature of the brickwork and rendering it more lasting.

The Solid Materials Fed to the Furnace. For the specific furnace chosen as example, the single charge weighs 23,700 pounds and consists of

Ore
$\left.\begin{array}{l}\text{Richmond ore ....} \quad 2000 \\ \text{Duane ore ....} \quad 1200 \\ \text{Carpenter ore ....} \quad 3200 \\ \text{Berkshire ore ....} \quad 3200 \\ \text{Hanna ore ....} \quad 2900\end{array}\right\}$ total 12,500 pounds

Briquettes, from flue dust (recovered ore).. 1,500
Limestone 3,000
Coke 6,700

Such a charge is carried by the skip hoist to the top of the furnace every 15 minutes during the 24 hours, with 2 periods left out, a total

FIGURE 260.—Section of the bosh wall in the blast furnace for iron, with 1, bustle pipe; 2, tuyere; 3, sight hole; 4, water-cooled metal boxes; 5, slag hole with water-cooled metal lining.
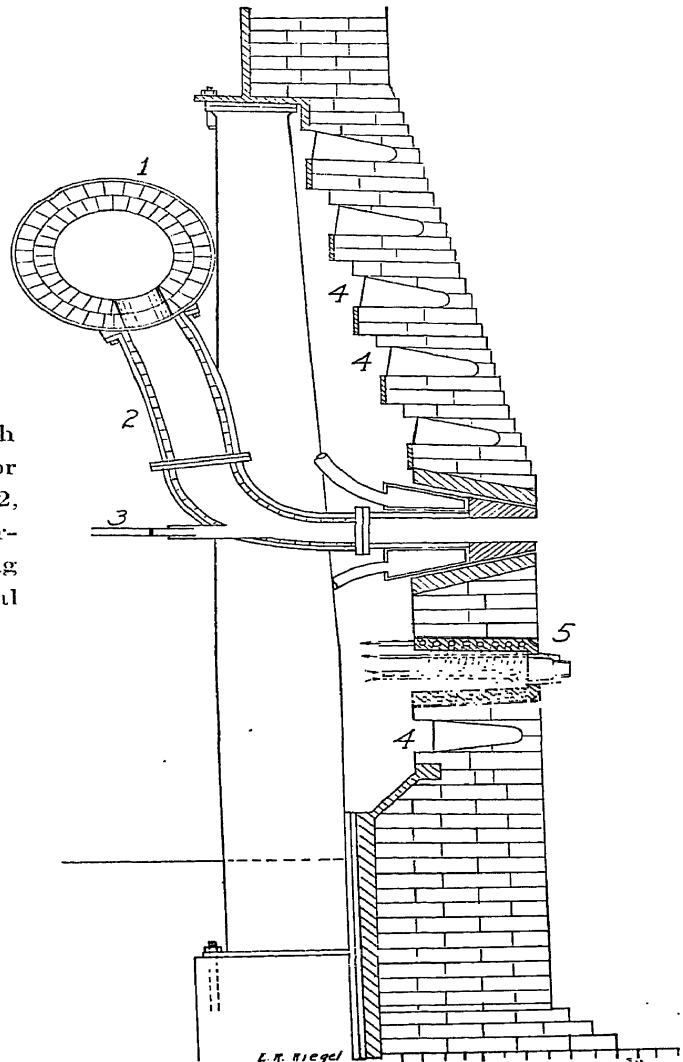
of 94 charges; total for the day, 2,227,800 pounds. Several skip-hoist buckets are required for each charge. The buckets are served from an electric larry which runs under a number of bins arranged in a row over the narrow-gauge rails of the larry; each ore is in a separate bin, also limestone and coke. The ore bins are filled from an overhead narrow-gauge electric railway which runs up an incline from the lower level of the yard. The bins are situated at one side of the ore piles, while open water is at other side, giving the ore boat access. An overhead crane travels over the ore, and by means of a clam-shell bucket loads the narrow-gauge cars. One of the bins contains the briquettes which are made from the ore dust recovered in the gas washer (mentioned again later). The coke is from an adjoining by-product plant, and is screened clean of dust and to egg size. The dumping of the skip-hoist car and the introduction into the furnace will be clear from the illustration and from previous statements.

The average consumption of ore per ton of pig iron made in 1935 was 1.70 tons, compared with 1.69 tons in 1934.[4a]

The Blast. Large as the amount of solids may seem, the air introduced exceeds it in weight. The air is pumped by two blowing engines, steam-driven, with reciprocating parts; the air cylinders are 84 inches in diameter, the stroke is 60 inches, and the speed is 41 r.p.m. The total weight pumped per 24 hours[5] is 3,660,000 pounds. This air is forced through one stove where its temperature is raised at first to 1800° F., then as time progresses, to a lower temperature, until at the end of an hour, the temperature is 1440° F.; the air is then turned into another stove, which in the meantime has been brought to the highest temperature. Four-fifths of the weight of air sent to the furnace is nitrogen, and takes no part in the reaction.

The Stoves. The stoves are tall steel chambers, lined and filled with a checker-work of fire-bricks, in which blast-furnace gas is burned with cold air for 3 hours; the bricks gain in heat. The cold blast from the engines is passed through for 1 hour, and after that time the gas is again turned on and burned. Each stove is being heated for 3 hours and gives up heat for a 1-hour period. If No. 1 is heating the blast, No. 2 is receiving its third hour's heating, No. 3 its second, No. 4 its first; they never cool down to a temperature much below 1440° F. (782° C.). The stoves in the instance chosen[6] have an internal downcome for the waste gases leading to a chimney, but in some constructions each stove is surmounted by a stack. It might be said also that instead of steam-driven blowing engines, gas-driven blowing engines with horizontal shafts have been very successfully applied.

Reactions in the Blast Furnace. The essential reaction, which is undoubtedly the net result of several others, is

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[4a] U. S. Bureau of Mines.

[5] Without counting out the two charges missed.

[6] These stoves are 22½ feet in diameter (circular) and 94½ feet high.

$$Fe_2O_3 + 3C = 2Fe + 3CO.$$

A large part of the coke merely burns in the blast to CO, thus furnishing the main part of the heat energy. It is very likely that free iron in the spongy form is first formed and melts only later when it passes through the lower part of the bosh; and it is also held that the first reduction is to a lower oxide, which is then later reduced to the metallic iron. The liquid iron contains carbon to the saturation point, in solution, and some in combination.

The limestone loses carbon dioxide, and the lime formed reacts with part of the silica to form calcium silicate:

$$CaO + SiO_2 = CaSiO_3.$$
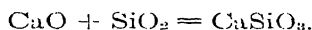
No appreciable amount of iron silicate forms because the lime displaces the iron, thus preventing a loss of metallic product.

The phosphate is present as calcium phosphate, and in presence of silica, the free phosphorus is liberated and dissolved by the iron:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = 6CaSiO_3 + 4P + 10CO.$$

Silicon is formed from such silica as may reach the hottest region where the combined action of iron and carbon reduce it to the free elements:

$$SiO_2 + 2C + (Fe) = Si + 2CO + (Fe).$$
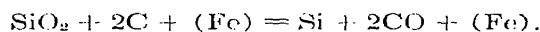
Manganese is reduced by carbon at the high temperature of the bosh. Both silicon and manganese are dissolved by the iron. Sulfur, partly if not all from the coke, forms ferrous sulfide which is so heavy that it mixes with the iron layer, and not with the lighter slag layer.

Tapping the Furnace. The furnace is tapped for iron every 4 hours. The iron hole is broken free of the dried clay, and the molten iron flows out along a gutter in the sand; it passes a small roughly made bridge with retaining box; under the bridge the clear iron flows on; over the bridge any slag which was entangled in the metal flows off through a sidewise gutter. The clear metal reaches a brick-lined steel ladle capable of holding 70 tons of metal; 60 tons are drawn at one tap. Near the end of the tap, the blast is shut off, and when the flow of metal becomes lazy, the clay plug is rammed into the hole. Operation is then resumed.

The slag is tapped every two hours, through its own hole, situated a quarter of a circle away from the iron hole, as well as further up. The slag is run through a gutter in the floor to a large container on a flat car and pulled to the dump heap, or to a near-by cement plant where it is granulated by cold water and used as one of the raw materials for making a Portland cement.

The daily capacity for this furnace is 357.6 tons [7] of pig iron, with the composition:

[7] The rated capacity of the 23-foot diameter furnace is 600 tons daily, reached whenever business demands it.

	Per Cent
Carbon	3.75
Silicon	2.50
Phosphorus	0.50
Iron	92.00

Casting the Molten Metal in Pigs. The ladle is tilted forward so that the metal is delivered to a box with two side outlets which divide the stream in two, and guide it to the little buckets of the two conveyors of a pig-casting machine. The belt conveyors travel as one, upward, as they leave the dividing trough. The rate of travel and the rate of flow of the metal are so regulated that the buckets just fill. Previously the buckets are sprayed with lime dust so that the new metal will not stick. A spray of water is played on the slowly traveling buckets, which congeals the iron sufficiently so that at the turn they drop off, still red, as cakes and slide into a waiting car, where they cool to blackness with the aid of more water. The capacity of a casting machine is high enough to cast all the metal from three furnaces of the size of the one just described. Each pig weighs 110 pounds and is 22 inches long, 7 inches broad at the base, and 4 inches thick.

In many blast-furnace plants, there is no need of casting the metal into pigs, for it is to be used at once for steel making in the open hearth, or in the Bessemer converter. For such purposes the iron is never taken directly from the blast furnace to the steel furnace or converter, but it is delivered first to a very large ladle capable of holding several taps; this large receiver is called the mixer. It offers the great advantage of furnishing a very uniform metal, avoiding single taps with just enough irregularity of composition to prevent the metal from giving the usual results. In some installations, the mixer is more elaborate still and the opportunity is taken to burn off some of the sulfur by playing a stream of burning gas over the surface.

The Blast Furnace Gas. The gas which passes out at the top of the furnace has been cooled considerably by the cold portion of the burden, which gains the heat which the gas loses. The gas is cold enough to be passed through a steel flue to a steel dust-catcher, and from there to a gas washer, a box through which a fine spray of water descends, while the gas ascends. The cleaned gas is made to work in several ways: to raise steam for the driving of the blowing engines, as internal gas fuel for the gas engines driving the air compressor, if such are used, and to heat the stoves so that by means of the latter the incoming blast may be heated. The gas is not rich in combustibles, but it contains enough to furnish the heat required for the purposes stated above; usually there is surplus gas, which in some cases is piped to households of employees. The heat value of the gas [8] is due to its carbon monoxide content:

[8] Other types of commercial combustible gases will be found in Chapter 15. Other analyses of blast-furnace gas will be found in *Chem. Met. Eng.*, **10**, 713 (1912).

	Per Cent
Hydrogen, H_2	1.0
Nitrogen, N_2	59.6
Carbon monoxide, CO	26.0
Carbon dioxide, CO_2	13.4
Btu. of the blast-furnace gas	87

The Temperatures in the Furnace. The outgoing gas leaves the top of the furnace with a temperature of 400° F. (204° C.); this may also be taken as the temperature of the upper part of the burden. As the burden travels downward, the temperature rises steadily and gradually to 2700° F. (1482° C.) at the wide diameter. The increase is then much more rapid; half way down the bosh, the temperature is 3150° F. (1732° C.), all the way down, facing the tuyeres, perhaps 3500° F. (1927° C.). The iron on the hearth is cooler; its temperature is about 3000° F. (1649° C.).

Improvements. An important improvement was the removal of water vapor from the air for the blast, by refrigeration (Gayley). At the temperature of the bosh, water vapor attacks coke, reducing the temperature; further up in the furnace, the heat is returned almost completely, but in a place where it is of no importance. This reduction in temperature is avoided by removing the water. Another advantage is that since humidity varies from season to season, the action of the furnace is irregular; this irregularity is removed by drying the air. The capacity of the furnace is increased; the coke consumption slightly decreased. There still are many furnaces, however, which use ordinary air; the introduction of the Gayley or other method of drying has not been universal.

Another improvement proposed is to enrich the air with oxygen from liquefied air.[9]

The making of castings of pig iron is described in Chapter 45.

The price for pig iron has varied considerably in recent years; a normal figure would be $20 a ton. A composite pig iron price for 1929 is $18.43 a long ton; for 1932, $14.00; for 1935, $18.03; for 1936, (estim.) $19.10. The quotation in February, 1937, is $20.75.

SPONGY IRON

Large-scale experiments in rotary gas-fired kilns in order to produce iron directly from the ore without first making pig iron have been successful. Ore and coke enter at the upper end; after drying, the reduction takes place in about 1 hour; the reduced product is discharged at the lower end. After cooling, the iron is separated from excess carbon and from ash by a magnetic separator. There is no fusion of the iron in the kiln, hence the fuel consumption is much lower. The permissible range of temperature is between 875° and 1025° C., with 950° C. the most desirable one.[10]

[9] *Compare* Chapter 19.
[10] *J. Iron Steel Inst.*, **111**, 491 (1925).

Wrought Iron

The earliest form of iron, obtained from the oxide ore by heating it with charcoal to the softening point, and then laboriously worked over ("puddled") at the heating place by handtools, with the metal never free from slag, lost its importance with the installation of the processes which produce liquid steel and liquid cast iron. Nevertheless, wrought iron is still being made, mainly because it has high corrosion resistance. Hand puddling was succeeded by mechanical puddling, itself supplemented by fagoting; the most modern and striking method, with rapid and high output, is the Aston [10a] process, also known as the Byers process.

Wrought iron is defined as a ferrous material, aggregated from a solidifying mass of pasty particles of highly refined metallic iron with which, without subsequent fusion, is incorporated a minutely and uniformly distributed quantity of slag. It is the presence of the slag which gives it its fibrous structure.

In the Aston process, the pig iron is melted in cupolas and blown in Bessemer converters according to the usual practice for steel (see next chapter). The blown metal is tapped into a ladle, then poured into molten slag contained in the processing ladle. The slag is held at a temperature several hundred degrees lower than the freezing point of the refined metal; the latter is continuously and rapidly solidified. Such rapid solidification causes the dissolved gases to burst out with sufficient force to shatter the metal into small fragments which settle to the bottom of the ladle, where they weld together, aided by slag particles, into a sponge. At once the excess slag is poured off, and the sponge ball (6,000 to 8,000 lbs.) dumped at the rate of one every five minutes on a platform of a 900-ton press, where it is squeezed into blooms ready for rolling.[10b]

Wrought iron has low carbon and low manganese content. For example, Byers No. 1 contains C 0.08 per cent, Mn 0.015 per cent, Si 0.158 per cent, P 0.062 per cent, S 0.010 per cent, slag by weight 1.20 per cent.

The production of wrought iron pipe and tubing, the most important outlet, was 35,879 tons, in 1935; the corresponding articles made from steel totaled 928,526 tons for the same year. Plates, sheets, bars, and other products are also made of wrought iron, to a limited extent.

Electrolytic Iron

Iron is deposited from a solution of ferrous chloride on the commercial scale; the purity of the deposit is essentially 100 per cent. Pyrrhotite, Fe_7S_8, or pyrite burned to FeS, gives, when treated with ferric chloride, ferrous chloride and sulfur. The solution is run to the electrolyzing tanks, in which rotating mandrils receive a coating of deposit which grows to the desired thickness. The tube is then stripped

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[10a] The patents granted to James Aston, on the manufacture of wrought iron, are: U. S. Patents 1,255,499; 1,413,513; 1,820,177; 1,890,637; 1,987,598; assigned to the A. M. Byers Company, Pittsburgh, Pa.

[10b] *See* chapter on "Wrought iron," by A. W. F. Green, "Metals Handbook," **1936**, Cleveland, O.; pp. 337-343.

off; it is very brittle because of dissolved hydrogen. The brittle metal may be powdered and pressed into a coil with the aid of some adhesive; such coils are valuable in electrical devices.[11] By heating the tube in a furnace, the hydrogen is driven out and the brittleness disappears. These tubes are made into seamless containers of small size. During the electrolysis, ferric chloride is formed, and this is the solution used on fresh portions of iron sulfide. This is the Boucher-Bouchayer process, developed at Grenoble, France.

OTHER PATENTS

U. S. Patent 2,057,919, influencing the chemical and physical properties of blast furnace slags; 1,984,793, production of pig iron and Portland cement in a blast furnace; 1,941,983, reducing iron ore; 1,964,402, same topic; 1,963,269 desulfurizing and purifying iron; 1,837,696, electro-thermic reduction of iron ores: Ore, carbon, and flux are introduced into a horizontal hollow graphite electrode; the charge is pushed gradually down the passage, gaining in heat, until the hottest zone at the mouth of the electrode is reached, where reduction takes place. The melted iron (cast iron composition) collects in a fore-chamber, which is tapped at intervals.

PROBLEMS

1. In the present chapter, is there an example of the countercurrent principle worth mentioning?

2. From the dimensions, stroke, and speed given in the text for the blowing engines, verify the value for the weight of air pumped in per day. Find first the volume at atmospheric pressure of the cold air used; each cubic foot weighs 0.0761 pound at 62° F.

3. Let the ore charged in the specific example for the blast furnace given in the text, contain 50 per cent Fe, and assume that the dust loss is nil, also that there is no other loss; compute the weight of iron which will be obtained, assuming the pig to be 92 per cent Fe.

4. Set up figures to show how many tons of the several materials are required to make one ton of pig iron, from information given in the text.

READING REFERENCES

"The blast furnace and the manufacture of pig iron." Robert Forsythe, David Williams Co., New York, 1909.

"The metallurgy of iron and steel," Bradley Stoughton, McGraw-Hill Co., New York, 1913.

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"Index to iron and steel patents," V. Everett Kinsey and Thomas E. Hopkins, American Compilation Co., Pittsburgh, Pa., 1931.

"Principles of the metallurgy of ferrous metals." Leon Cammen, American Society Mechanical Engineers, New York, 1928.

"Slag viscosity tables for blast-furnace work," Bur. Mines, Tech. Paper 187, 1918.

"The basis for desulfurization of pig iron and steel," P. Bardenheuer and W. Geller. *Kaiser Wilhelm Inst. Eisenforchung*, Düsseldorf, 16, 77-91 (1934).

"The iron furnace," T. L. Joseph, *U. S. Bur. Mines I. C.* 6779, (May, 1934). See also *R. I.* 3229, and *R. I.* 3240.

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[11] Such a coil has low hysteresis losses, and is used as the Pupin coil.

The production of steel in 1935, for the United States, was 34.4 million long tons (2240) pounds; for 1933, 23 million. The making of steel on this huge scale is an industry only about 72 years old; it dates from the invention in 1855 by Henry Bessemer, an Englishman, of a new method of purifying pig iron, the usefulness of which was extended (1878) by Thomas and Gilchrist, also Englishmen. The process of Bessemer was discovered independently by William Kelly, of Kentucky, in 1847.* The other main process for steel is due to William Siemens, an Englishman, and to E. and P. Martin of France (1865). Several of the important improvements of a later date are due to Americans.

Chapter 48

Steel

Steel is a purer iron than cast-iron; the undesirable impurities of the latter, silicon, phosphorus, sulfur, and manganese, are either removed or reduced to a very low amount; carbon, which is 2.5 to 4 per cent in cast iron is reduced to 0.2 per cent for a very soft steel, 0.55 for rail steel, and perhaps 1 per cent for extra-hard steel, in all cases distinctly lower than in cast-iron. It will be noted that the amount of carbon in the steel, varying between the comparatively narrow limits of 0.20 to 1 per cent, regulates the hardness of the steel. The manufacture of steel is then essentially a purification of pig iron, by slagging the phosphorus, silicon, and manganese, and removing the excess carbon by oxidation; the raw material is not pig iron alone, but to large extent steel scrap of all kinds. The proportions of pig iron and scrap are not fixed but depend upon market conditions. The removal of the impurities effects a profound change in the properties of the material; the brittle, comparatively weak cast-iron, which cannot be rolled, is transformed into the strong, tough steel, which may be rolled and forged while at red heat; the melting point rises. Table 78 shows the difference in some of the properties:

TABLE 78.—*Properties of Iron and Steel.*

	Specific Gravity	Tensile Strength per sq. inch Pounds	Melting Point ° F.	Melting Point ° C.	Carbon Content *Per Cent*	May Be Rolled
Pig iron (gray)	7.3	15.000	2000	1093	2.50–4.00	No
Medium steel	7.8	65.000	2500	1371	0.15–0.30	Yes
Rail steel	7.8	110,000	2500	1371	0.55	Yes

Steel has the further advantage of acquiring a "temper," varied according to the details of treatment, by heating and quenching; heating and slow cooling removes the temper.

* U. S. Patents to William Kelly, 16,444 (1857), combination of the hearth of a blast furnace with auxiliary tuyeres bringing a blast of air; 17,628, blowing blast of air, hot or cold, through a mass of liquid iron, the oxygen combining with the iron, causing a greatly increased heat and boiling commotion in the fluid mass and decarbonizing and refining the iron; 18,910, claim 1, conducting a blast down through the liquid iron to near the bottom of the hearth; claim 2, refining and decarbonizing simultaneously in the hearth of a blast furnace and in an adjoining chamber having communication therewith.

The steel produced on a large scale has become a structural material of first importance, replacing stones and bricks, and making possible the building of bridges which otherwise would not exist. The American skyscraper would have been impossible without steel. The extension of railways is due also to the large-scale production of steel, not only for the rails, but also for the locomotives. Stationary high-pressure boilers, steam engines and turbines, machines of all kinds depend upon the production of steel. The two processes by which such steel is produced are the Bessemer converter process and the open hearth process; the two produce essentially the same kind of steel.

There are in addition a large number of special steels, with properties suiting specific purposes, many of them of great importance, although the tonnage used may be small. Examples are: self-hardening tool-steel, nickel steel for armor-plating, chrome steel for navy guns; these will be described briefly further on, and also the process of combining a hard surface with a tough, strong interior, by case-hardening.

Open Hearth Process

The open hearth process was introduced some 10 years after the Bessemer converter. The charge is placed on the hearth of a large brick furnace heated by gas or oil fire, and the heating continued, with occa-
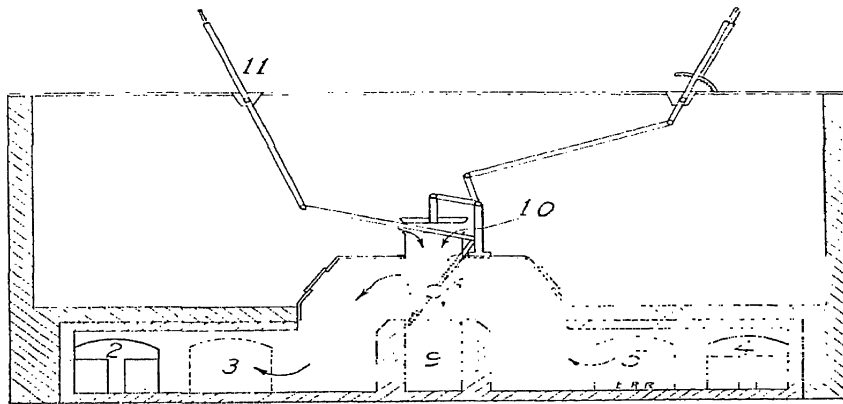
Figure 261.—Air reversing mechanism; 10, entering cold air; 3, regenerator for preheating the air; 5, fire gases leaving the second regenerator for air, and passing to the stack at 9; the butterfly valve is reversed at 11. A valve for controlling the amount of air is also provided.

sional additions of fluxing materials, until the carbon is sufficiently low; the product is tapped at intervals.

As example of open hearth furnace practice, a specific furnace with a hearth 19 feet broad by 34 feet in length, with a capacity of 100 tons every 11 hours, will be described. The hearth is on a level with a work-
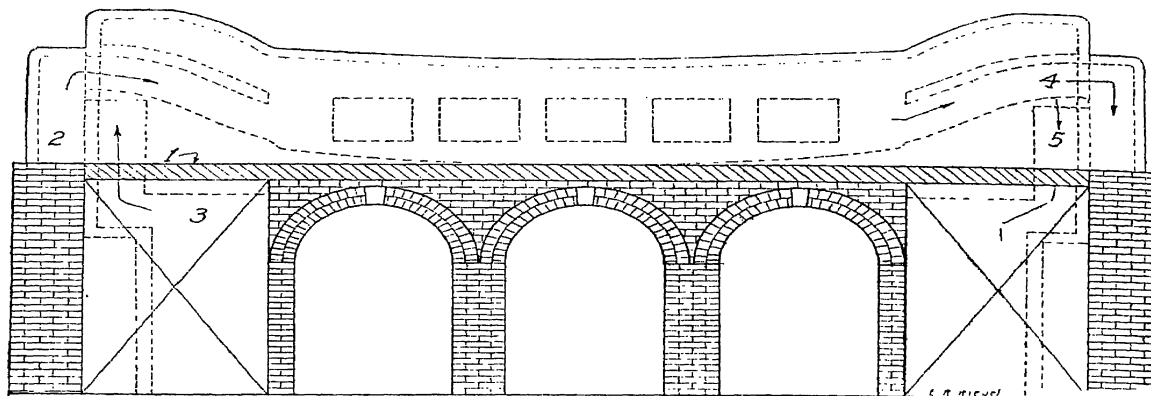
FIGURE 262.—Front view (elevation) of the open hearth furnace for steel. 1, working floor; 2, entering hot producer gas; 3, entering hot air blast; 4, fire gases passing to regenerator for gas, and 5, for air. The same numbers for blast and air are used in the several sketches.

ing floor sufficiently elevated so that on tapping, the metal may be run into a receiver, the ladle, standing on the ground floor; this provides at the same time space under the furnace for the brickwork of the regenerators. The fuel is producer gas,[1] preheated in a regenerator; the air is also preheated. Air and gas enter by separate ducts at the left of the
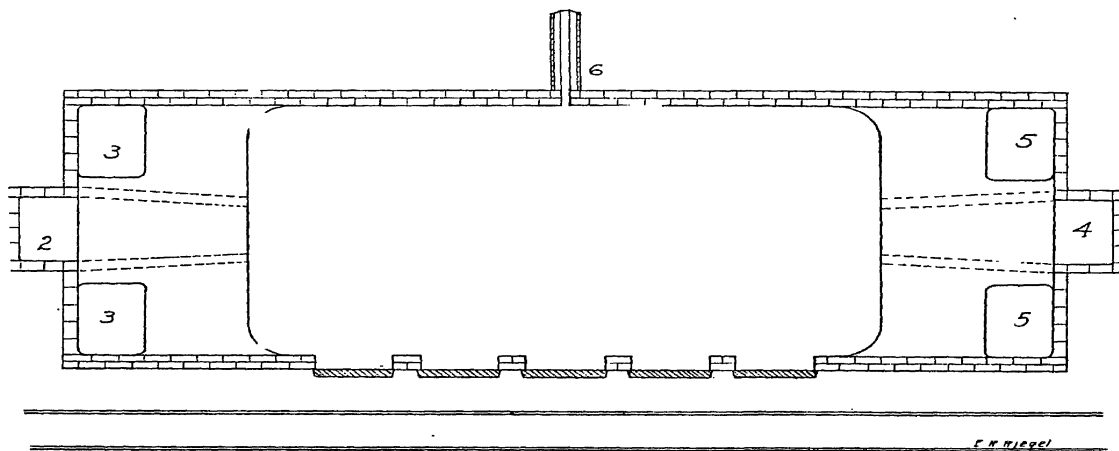
FIGURE 263.—Floor plan of the open hearth furnace; 2, gas entry; 3, air entry; 4, fire gases to gas regenerator; 5, fire gases passage to air regenerator; 6, tapping trough, at the rear of the furnace.

furnace, mix, and sweep while burning over the hearth, and pass out at the right, reaching two regenerators which they heat, before escaping to the stack. There are in all 4 regenerators to each furnace; the direction

[1] Chapter 15.

of the gas and air is reversed every 15 minutes, by hand operation of levers which control the compressed-air mechanism which swings the valves. A scheme for the reversal of the air is shown in Figure 261; a second similar arrangement reverses the gas flow. Several views of the furnace (Figs. 262-264) will add to the description. The roof of the furnace is rather high (8 feet) in order to give room for the charging pans. The doors are water-cooled steel doors, operated by compressed-air mechanism with distant control.

The furnace has 5 working doors which face the working platform; all the work is done on this side except the tapping, which is done at the rear (*compare* Fig. 264). The furnace floor is built of clay bricks, covered with magnesite bricks,[2] and these are covered with magnesite
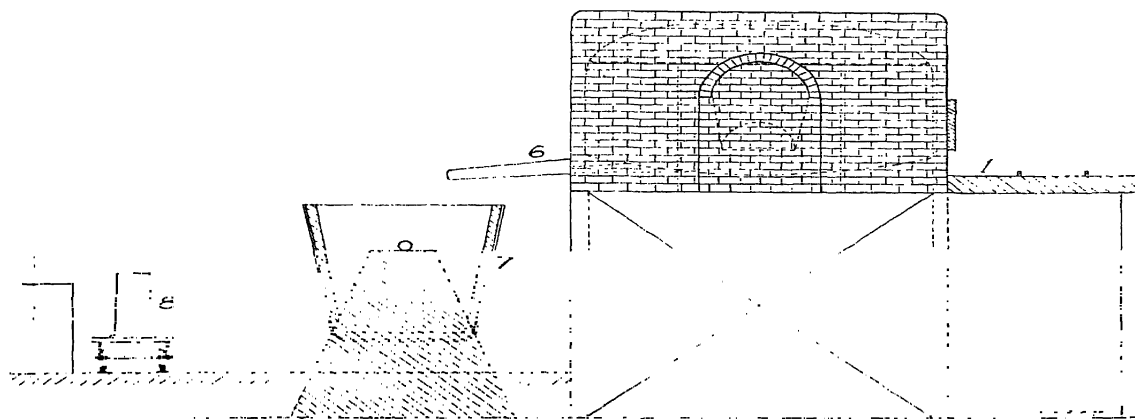
FIGURE 264.—Side view (elevation) of the open hearth furnace, showing the relative location of working floor 1; tapping trough 6; ladle 7, and ingot mold 8.

lumps of assorted sizes mixed with 15 per cent basic slag, well burned in. The roof is lined with fire-bricks. On the floor, calcined dolomite is thrown by hand shovels before every charge, and the furnace is then ready for the run or "heat." The charge consists of

>125,000 pounds of scrap iron, mainly ends of sheet steel
>25,000 pounds of cold pig iron, from the storage pile
>100,000 pounds of melted pig iron just from the mixer
>26,000 pounds of limestone
>500 pounds of fluorspar added at intervals during the 11 hours
>2,000 pounds of iron ore, such as hematite

The cold materials are in narrow pans, 4 to a truck (rails). A steel housing moves on rails along the platform, and lifts each pan, pushes it into the furnace through the opened door, rotates it to dump the contents, and pulls it out again, by means of a mechanical arm with inside movable rod; the pan casting has the necessary slots to receive the arm

[2] 90 to 93 per cent MgO.

lock. The hot pig is poured from a ladle hung from an overhead crane into a trough at one of the working doors. After all the materials have been added and have melted, the depth of the liquid metal on the hearth is about 24 inches. With the charge in the furnace, there is little to do except to reverse the gas flow and observe the progress of the reaction, until near the end of the period.

The relative amounts of pig and scrap vary. It may be 40 per cent pig as liquid iron, tapped for example from the mixer at the foot of the blast furnace, which holds 3 or 4 blast furnace taps, and 59 per cent scrap, with perhaps 1 per cent ore added merely in order to reduce the great amount of carbon which the pig iron brings. Or, it may be the "pig and ore process," with 70 per cent pig, 30 per cent scrap, and 12 per cent iron ore based on the metal and scrap. In this latter case, a sizable portion of the final steel come from the ore directly.

It will be well to remember that in any case a vast amount of carbon is brought to the furnace, and the essential function of the open hearth becomes the removal of any excess carbon by combustion, along with phosphorus, sulfur, and silicon.

Progress of the Heat. The operator observes the appearance of the mass at the peephole in each door, through blue glasses. The temperature is 2400° F. (1315° C.) at first, and increases to 2800° F. (1538° C.) and even 3000° F. (1649° C.); after a time, the charge is melted and the liquid appears to boil violently. A part of the boiling effect is due to the escape of gases occluded in the metal, a part to carbon dioxide escaping from the limestone, and another part to the carbon monoxide from the carbon in the pig iron, burning with the oxygen of the hematite and of the furnace gases. There are two ways for the rapid determination of the amount of carbon still present in the metal. The older way is to take a spoonful of metal and to pour it into a mold to form a small pig which is quenched and then broken in two. From the appearance of the fracture, the trained eye of the operator can tell the carbon content with remarkable accuracy. The latest method is the carbometer,[2a] an instrument which measures the magnetic induction in a rod of steel cast from the metal in the furnace. With a few motions and in less than a minute, the "melter" knows the carbon content within one point (0.01 per cent C.). Besides these rapid tests, it is not infrequent to hold the furnace quiet while an analysis is made in the nearby laboratory. After 11 hours, the carbon content has been reduced to the desired point and the furnace is ready to be tapped.

Over the liquid metal there collects gradually a layer of slag, containing the impurities. Oxidized silicon and phosphorus form, with the lime from the limestone, calcium silicates and phosphates, which are melted and float on the metal, because their specific gravity is lower. The fluorspar is added to make this slag layer thinner, more readily separated from the steel.

[2a] The carbometer is described briefly in Chapter 46. A set of curves giving carbometer readings against per cent carbon appears on p. 162, *Metals Progress*, **31**, (1937).

The changes in the basic open hearth furnace are indicated in the figures below.

Changes in Basic Open Hearth Furnace.

	Charge	Steel
	——————Per Cent——————	
Carbon	1.0	0.18
Silicon	1.40	.004
Phosphorus	0.05 to 2.5	.02
Manganese	1.80	.44
Sulfur	.1	.042
Iron	93.2	99.3

Tapping the Furnace. A ladle with the capacity of 100 tons (15 feet high) of brick-lined steel, with nozzle in the bottom, has in the meanwhile been placed in position at the rear of the furnace. The tap-hole is cleared by a bar and a stream of oxygen; if the hole does not form, a small pig, red hot, is brought from the front of the furnace and placed in the taphole; a stream of oxygen is played on it and the high temperature so produced melts the cold steel and opens the hole. The steel at white heat flows out through a short trough into the casting ladle; slag runs out near the end and is run off from a side trough at the top of the ladle and forming part of it. The ladle is lifted by an overhead crane traveling in the rear of the furnaces, and carried over the ingot molds.

Casting Steel Ingots. The ingot molds are made of cast iron, open at top and bottom; they are set each on a heavy steel or copper base plate, carried on narrow trucks on rails, 6 to a truck. The bottom of the mold is formed by the heavy base plate; a little sand at the edges prevents the metal from running out. The ladle is brought over the mold, and the fire-clay plug lifted from the fire-clay nozzle in the base by a rod (with protecting fire-clay sleeve) operated from a second rod running down the side of the ladle. After one mold is filled, the plug is lowered into place, and the ladle is moved to the next. Each ingot weighs about 2½ tons, is 19 inches square (with rounded edges) and about 5 feet high.

An improvement in the casting procedure consists in placing over the top of the mold a stoneware sleeve as wide as the mold itself, and allowing the metal to rise within it. This "chimney top" does not chill the metal, allows the gases to escape, and prevents, by feeding hot molten metal downward, the large cavity formerly formed in the upper part of the ingot. A further advance is "scarfing", namely, cutting away with an acetylene torch the bad metal from the corners of the ingot.

Rimming Heat. There are to be distinguished the "rimming heat," the "killed heat," and an intermediate one. The rimming heat may be illustrated by a manganese rimmer, a steel to be used for nuts and bolts stock. Such a steel must contain sulfur, which may be as high as 1 per cent; in this case it will be more moderate. During the progress of the melt of 100 tons, there will have been added 1000 lbs. of manganese; and while the tapping is in progress, there are added to the ladle, which takes the whole of the "heat," that is, of the tap, 300 lbs. of brimstone, 60

lbs. of anthracite to restore carbon and bring it to the required percentage, and finally 1400 lbs. of manganese in the form of 80 per cent (ferro-) manganese. The resulting steel contains, in this case, 0.16 to 0.18 per cent C, 0.55 to 0.65 per cent Mn, 0.10 to 0.12 per cent S. As the steel is poured from the ladle into the ingot molds, the liquid steel works, that is, bubbles, for several minutes. On cooling, the ingot will be found to have a crust of close-grained metal along the outer walls, with a core or coarser grained metal, darker in color; hence the appellation "rimmed." The ingot passes through the blooming mills, and is reduced in size in other mills, undergoing continually an elongation, but never losing this composite structure of fine grained rim with coarser grain core. The purpose of the sulfur addition, and other additions in definite proportions, is to produce a steel which will give short turnings when threaded, which then fall off easily and do not plug the dies in the automatic screw-making machines. The sulfur is present in the form of manganese sulfide. The steel just described is for "hot heading" such nut and bolt stock; a somewhat different composition is selected for the "cold heading" stock, with the carbon .15 per cent and the manganese somewhat higher.

Killed Heat. A high manganese steel will illustrate the "killed steel;" such a steel might be spoken of also as a high-impact steel. The bath in the open hearth furnace is brought along in the usual way, with the addition of a certain amount of ferro-silico-manganese (66 per cent Mn, 18 per cent Si). Near the end of the period, there is added a "wash" of pan pig iron; these sink in the melt, and cause a violent action from below which drives upward any sluggish impurity which is to be slagged. Next for a "block," some 3000 lbs. of silicon-manganese iron are fed in. This addition melts and quiets the bath, giving an interval with essentially no "work," hence no change in composition; that period is utilized to make a laboratory analysis for carbon and manganese. It should be said that the quietness of this interval is helped by shutting off the gas and air. Guided by the analysis, the proper amount of 80 per cent manganese is placed in the furnace, and it is ready for tapping. To the ladle, as it fills, there may be added anthracite. The final composition is 0.30 per cent C., 1.65 to 1.75 per cent Mn, not over 0.03 per cent P, not over 0.04 per cent S. As the ladle is lifted over the ingot molds and fills these, the steel does not "work" at all; it is quiet, and begins to solidify at once; all action in the ingot mold has been "killed." The metal is essentially uniform over a cross-section. This steel fits S.A.E. T1330.

For this high manganese "killed" steel, the hot top chimneys are used over the ingot molds.

Soaking Pits. The small trucks with the filled molds are pushed under a shed in which an overhead crane travels, which carries special lifting claws fitting the mold. The claws engage the mold and lift it up, leaving the ingot (still red) standing on the platform; the mold is placed on an empty truck ready to return to the furnace building. Any mold which fails to leave its ingot is reworked in the furnace, mold and ingot. The stripped ingots are conveyed to the mill building, and first reheated

to bright red heat in the "soaking pits" (2 hours or less). The pits are brick-lined chambers in the floor, 6 feet deep and 4 by 6 feet in cross-section, heated by gas. As a rule, four pits are served by one gas main.[3] The transfer of the ingots to the pits and their removal is done again by an overhead crane, carrying a grabbing tool (the dog). The reheated ingot is deposited in a steel basket on an electric truck, which carries it to the first of four or five mills, where a trip dumps the basket, so that the ingot lies on its side ready to enter between the two rolls of the mill.

Rolling Mills. The ingot enters the first set of rolls of the mill (sometimes called the blooming mill) which reduces its thickness; it is returned to the rolls after being turned on its other side by mechanical claws, so that all four faces are pressed; it is at the same time elongated. This treatment is repeated in the next set of rolls, the steel billet lengthening at each passage while its diameter diminishes. In order to make steel rails, the rolls have grooves arranged so that two which revolve on each other leave a passage approaching the shape of the rail cross-section; the last passage has exactly the shape of the rail. The imperfect ends are cut off by heavy shears and returned to the open-hearth furnace. Each mill has two (or three) horizontal rolls, with several grooves for the smaller rolls, of gradually diminishing size; the steel may be passed back through the same rolls, forward again and back again, a number of times, each time through a smaller passage; the method of moving the steel is by smooth rollers forming the floor on which the piece rests; the floor rollers may be revolved at any speed, and may be reversed at the will of the operator, who stands at a dis-. tance on the control platform. The floor rollers as well as the mills are driven by steam engines or D. C. motors, through gears with V-shaped teeth. To keep the mill rolls from heating, a small stream of water is allowed to flow over them; some of it reaches the steel, but has no appreciable effect.

As the steel rail emerges from the last passage, it travels to a revolving saw which cuts its end true; it then moves on to a stop which controls its length; the saw makes another cut. A second length is measured off and cut, and the waste end sent back to the furnace. The rail, which is still red hot, is moved to a storage shed (floor rollers), where floor claws push it along resting bars toward one end of the room, to cool. One ingot of the size given makes two rail lengths, and the time required from the blooming mill to the shed is about 15 minutes.

Not only rails, but flat iron, bars, angle irons, tees, channels, and I-beams are shaped in this way. Wide flat iron (skelp) is bent and welded to form tubes (iron pipes of all sizes) by automatic operations.[4]

The process of rolling is not merely a shaping of the mass, but because of the pressure applied in the mill, the particles in the steel are pressed

[3] A sketch of the soaking pit will be found on p. 219, "The metallurgy of iron and steel," by Bradley Stoughton (*see* reading references).
[4] The National Tube Co., McKeesport, Pa.

together, coarse particles destroyed, and the strength of the material increased.

A distinction is made between the basic open hearth and the *acid open-hearth process;* in the basic open hearth, which is the more important one, pig iron and scrap containing 2 per cent of phosphorus and even more may be used, for by the addition of lime, this phosphorus, after oxidation to its oxide, is fluxed out as calcium phosphate. The acid open hearth, the original process, makes no provision for the removal of the phosphorus; pig iron or scrap with a low phosphorus content must be used (0.045 per cent P), and the steel will contain a slightly higher percentage. The acid open hearth is used in England. Four-fifths of the rails produced in the United States are open-hearth steel.

Continuous Strip Mill. Increased demand for sheet steel has made a more rapid and more economical method of production desirable, and this has been realized in the Mesta machines, which roll a slab into a continuous sheet of steel at a rate not unlike the rate of paper-making on the Fourdrinier.

A slab, let us say for illustration, 35 inches wide, 13 feet long, $4\frac{1}{2}$ inches thick, of low carbon steel, preheated to 2300° F. (1260° C.), is pushed (mechanically) onto rollers forming the first part of a long roller platform interrupted only by the rolling mills. From here on, the steel travels in a straight line, in one direction. The slab is fed successively to each of 4 stands called "four highs," each operated as single units and at individual speeds. Each "four high" rolling mill consists of 4 rolls, arranged vertically; reading from the bottom up, they are: an idler, a driven roll in contact with it, the gap through which the steel passes, an upper driven roll, and finally another idler, the "back-up." A scale breaker strikes the slab as it moves from the first to the second of these preliminary stands. Beyond the fourth stand, the slab reached a space called the "cooling table," where it can be moved back and forth until it has cooled to the proper temperature for the final pass, namely 1620° F. (882.2° C.). The slab is, by now, considerably elongated, and much thinner, perhaps $\frac{3}{4}$ inch. It now enters the first of a set of 6 stands, also "four highs," passing directly from one to the next and emerging from the last, with the prescribed thickness or gauge. These 6 "four highs" reduce the thickness of the steel stepwise; they have different speeds of rotation [4a] taking up exactly by the increment in speed the increment in length. The width is set by side guides. The still red sheet hurries down the long table (with driven rollers for floor), to wind itself automatically into a coil, which is pushed out and dumped onto a floor conveyor traveling at right angle to the long table.

The maximum speed on leaving the last of the 6 "four highs" is 1350 feet per minute, for the lowest thickness (.050"); the minimum speed for the heavier gauges is 200 feet. For the medium thicknesses it is around 500 feet; this means that the observer, standing on the bridge over the hot

[4a] Thus for number 6, the final mill, 190; number 5, 160; number 4, 108; number 3, 90; number 2, 64; number 1, 46.

table, will see the red sheet rush by below him in 30 seconds, for a length of 250 feet,[4b] a frequent length. The time from slab to coil is 2 minutes.

The clearance at the last mill is still much greater than the thickness of the steel; for example, a clearance of .220 inches is used to produce a sheet .074 inches in thickness.

The hot mill capacity is 50,000 tons a month. The width of the sheet may be as high as 72 inches.

After cooling, the coil is passed unwound through the pickler (dilute HCl), is washed, dried, and oiled, and next *cold rolled*, with a reduction in thickness of 60 per cent. This considerable reduction is accompanied by the creation of strains, and brittleness, so that the cold rolled sheet, now cut in convenient lengths (a popular size is 68 inches by 120 inches), is made into piles and covered with an annealing oven. The atmosphere of the oven is controlled; the box is filled with DX gas in order to deoxidize the surface, and restore a shiny non-scale surface; the heating is indirect. After 72 hours, the pile of sheets is allowed to cool, and may then be cold rolled again, this time with no reduction (skin roll). The sheet is then inspected under a mercury arc for seams, stretcher strains, buckle, gauge and other particulars.

A part of the hot rolled steel is used as such, for the manufacture, for example, of automobile chassis frames, exhaust pipes, tubes for the differential housing.

The Bessemer Converter

Acid Process. The Bessemer converter is a pear-shaped vessel with perforations (the tuyeres) at the bottom through which a blast of cold air (pressure 25 pounds) may be introduced; molten pig iron from a mixer is poured in and blown for a period of about 20 minutes; the silicon and manganese are oxidized and combine with that portion of the iron which is oxidized at the same time. In the simplest case, that of the acid Bessemer process, three periods may be distinguished. In the first, slag forms; in the second, the liquid "boils," the carbon is burned and escapes first as dioxide, later as monoxide (CO); it is the escape of the latter gas which causes the "boil." The flame at the mouth of the converter during the second period is large. The third period is the finishing period, when the last of the carbon burns to monoxide; as its amount diminishes, the flame dies down. Much heat is produced during the blow, mainly by the burning of the silicon (*compare* Problem 2); in fact, the Bessemer conversion succeeds best when there is a 2 per cent content of silicon in the pig iron; with a lower content, 0.8 or 1 per cent, the converter must be kept hot by rapid working. The blow over, an addition of spiegeleisen [5] is made in the converter, and a short afterblow is applied; the manganese reduces any oxide of iron

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[4b] The length of the rolled sheet may be computed by dividing the proposed thickness in inches, into the thickness of the original slab, and multiplying by the length of the slab; width to remain the same.

[5] Spiegeleisen means mirror iron; it is a low-manganese iron alloy; Mn 15%, C 4.5%, Si 0.5%, Fe 79.7%, S 0.2%, P 0.28%. The amount added is 6% of the charge, or even more.

which has been formed and at the same time furnishes carbon, which the main blow has practically completely removed.

A Bessemer converter for a 10-ton charge is about 15 feet high, mounted on trunnions, and elevated sufficiently to allow the pouring of the finished steel into a ladle. The converter is lined with acid (silica) bricks, and has a removable bottom piece, which lasts only 12 to 15 blows, and a removable nosepiece.[6] Other details are indicated in Figure 265. Converters large enough to hold 20 tons are not uncommon. The charge occupies only one-sixth of the space within the converter, to allow for agitation. The pig iron or melted scrap must contain not more than 0.05 per cent phosphorus.
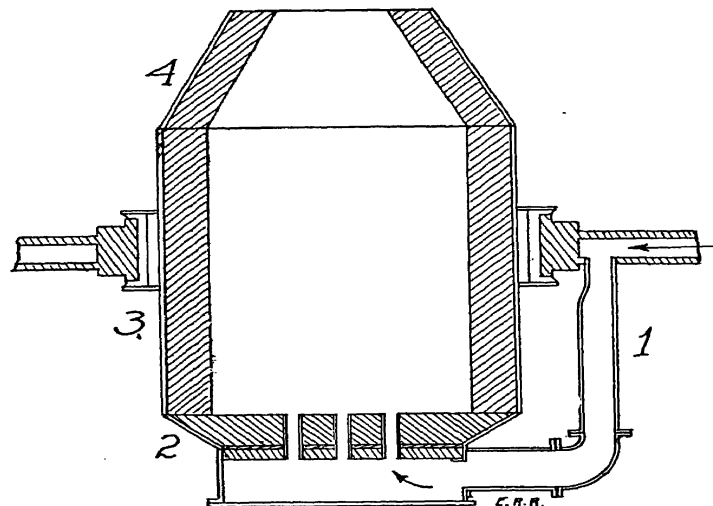
FIGURE 265.—The Bessemer converter for steel; 1, entry for air blast, cold; 2, bottom piece; 3, body; 4, nose piece of the converter. The tuyeres are shown in 2.

Basic Bessemer Practice—The Thomas-Gilchrist Process. The basic Bessemer conversion differs from the acid Bessemer just described in several particulars. It is devised for phosphorus-containing pig iron, or melted scrap, and during the blow, it is the burning of the phosphorus[7] which furnishes the heat, instead of the silicon; the phosphorus content is usually 2 per cent, and may be as high as 3 per cent. Lime is added, in lump form, in order to bind the phosphorus oxide, P_2O_5, as calcium phosphate; and as such basic material as hot lime would speedily ruin the silica brick lining usually applied to the acid converter, the lining must be different, namely basic. It is made of dolomite bricks. The amount of slag formed in the basic Bessemer is greater than in the acid one, and for the same charge of metal the converter must therefore be somewhat larger. Finally, the spiegeleisen is added only after the metal is in the ladle, so that a reduction of the phosphate

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[6] The nosepiece lasts 50 blows; the body, 200.

[7] For heat value, *compare* Problem 2.

by the carbon in the spiegeleisen may be prevented. The basic Bessemer is much used in France and Germany, less in the United States.

The composition of the charge and of the product for the two Bessemer processes are given in Table 79.

TABLE 79.—*Composition of Charge and Product.*

	Basic Bessemer Process			Acid Bessemer Process		
	Charge	Steel	Undosed**	Charge	Steel	Undosed**
		—Per Cent—			—Per Cent—	
Carbon	3.60	0.20	(trace)	3.50	0.20	(trace)
Silicon	0.61	0.01	(0.005)	2.10	0.02	(none)
Phosphorus ..	2.52	0.04	(0.04)	0.04	0.045	(0.045)
Sulfur	0.07	0.05	(0.05)	0.04	0.044	(0.044)
Manganese ...	1.45	0.40	(0.12)	0.45	0.48	(trace)
Iron	91.75	99.30	(99.7*)	93.87	99.21	(99.8*)

* Iron oxide is present.   ** That is, before correction by spiegeleisen addition.

Both steels given in the table would be mild steels for general structural purposes. The reactions are violent; the pig iron is changed to the pure iron shown under the column "Undosed"; such iron has the fatal defect that it contains iron oxide, which renders the product almost useless. The addition of the ferromanganese or spiegeleisen removes the oxide of iron, for the manganese combines with the oxygen of FeO with great rapidity; at the same time, carbon is furnished to reach the designated percentage. That the very pure undosed metal is fluid means that a very high temperature is produced in the converter.[8]

It was the invention of the use of spiegeleisen as a deoxidizer and at the same time recarburizer which saved the Bessemer process from failure in its early days (Mushet, 1856). Other deoxidizers are ferromanganese alloys with 40 to 80 per cent manganese; also silicon alloys and aluminum.

The composition of structural steel need not be those given in the table above; in the case of the towers for the George Washington Bridge over the Hudson, at 178th Street, New York City, the steel used contained about 0.27 per cent silicon. The high silicon content was selected in order to improve the physical properties of the steel, not for the purpose of decreasing any possible corrosion.[9]

Slag. In the acid processes, the slag is due to the burning of the silicon, Si, to silica, SiO_2, of the manganese, Mn, to the oxide, MnO, and of some of the iron, Fe, to FeO; these react further to form manganese silicate and iron silicate:

$$MnO + SiO_2 = MnSiO_3; \quad FeO + SiO_2 = FeSiO_3.$$
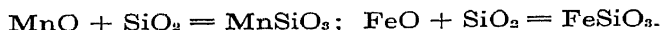
In the basic processes, the phosphorus, P, burns to the pentoxide, P_2O_5; some iron to its oxide, FeO, and the manganese again to MnO; there is

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[8] The purer the iron, the higher its melting point. No fuel is needed in the Bessemer conversion; as indicated before, the heat is due to the oxidation of the silicon (acid process) or the phosphorus (basic process).

[9] Private communication, The Port of New York Authority, Herbert J. Baker, engineer of steel inspection.

then formed calcium phosphate,[10] essentially, containing iron phosphate and some manganese phosphate:

$$3CaO + P_2O_5 = Ca_3(PO_4)_2.$$
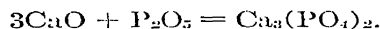
The liquid slags are lighter than the melted steel and float on the latter.

A continuous open-hearth process, in which 20 tons of steel are tapped at intervals from a total charge of over 100 tons, is in operation (Talbot);
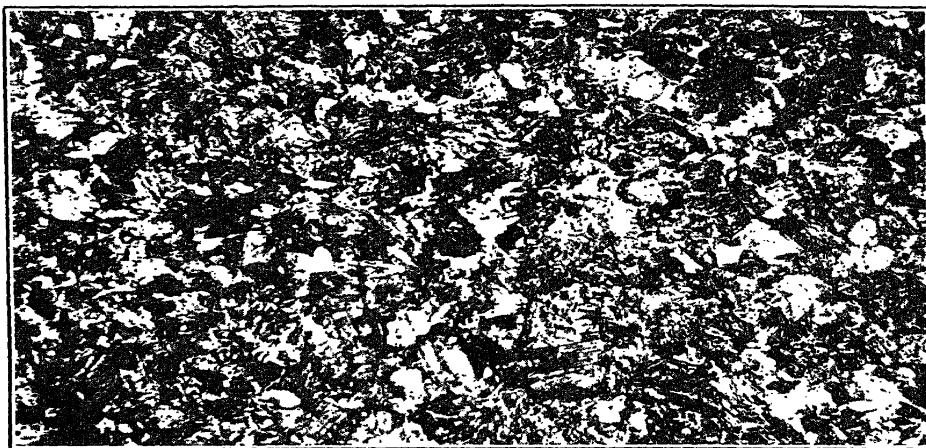
FIGURE 266.—Photo-micrograph of a polished surface of high-carbon steel, etched magnified by 250. The dark areas are pearlite; the light areas are cementite.

the main advantage is that the bottom of the furnace remains covered by the steel and is not attacked (or very little) by the slag.

Sulfur may be slagged out by means of manganese, which forms manganese sulfide, MnS.

SPECIAL PRODUCTS

Nearly pure iron was made formerly from very pure raw materials, and with charcoal; it is possible to make surprisingly pure irons in the open-hearth process by holding the charge for some time longer in the furnace to lower the content of silicon and manganese; at the ladle aluminum (shot) is added liberally, perhaps $1\frac{1}{2}$ pounds to the ton of iron. The Armco brand of iron, used for cornices and conductor pipes, is such an iron; it rusts either not at all or very slowly; its composition is carbon 0.02 per cent, manganese 0.05, silicon 0.01, phosphorus 0.01.

Steel is iron containing carbon, in part as iron carbide, Fe_3C, called cementite; in part free, as graphite; the total amount for steel lies between 0.135 and 1.5 per cent C.[11] Heated and suddenly quenched, it becomes more elastic, harder, and more brittle; these qualities may be varied for

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[10] For the use of basic slags as fertilizers *compare* Chapter 18.
[11] Iron with 2.5% carbon and more is pig iron.

any one steel by varying the temperature and the period of quenching. Most of the iron is free, and occurs as ferrite, of which there are three varieties. On cooling a piece of steel and observing its rate of cooling by means of a pyrometer, it is found that the cooling is not regular and gradual but is arrested, and the steel remains at certain temperatures for a little while; this is due to the change of one form of ferrite to another, which takes place with evolution of heat. By heating to a predetermined temperature and cooling suddenly, the structure existing at that temperature may be preserved, with the properties which accompany it. A steel with 0.89 per cent carbon consists entirely of "pearlite", which is made up of thin parallel plates of cementite and ferrite side by side (a eutectic mixture); above 0.89 per cent carbon, there is a network of cementite around pearlite beads; below 0.89 per cent, ferrite is mixed with pearlite. "Austenite" is a solid solution of cementite in iron (ferrite). The structure of the steel may be studied by means of the microscope with photographic attachment.[12]

Steel is made into a number of forms suitable for certain uses. For example, in the following list, which has also the quantity in thousands of long tons for the year 1936 (U. S.), for companies having 94.3 per cent of the total ingot producing capacity: rails, 1,157; track accessories,
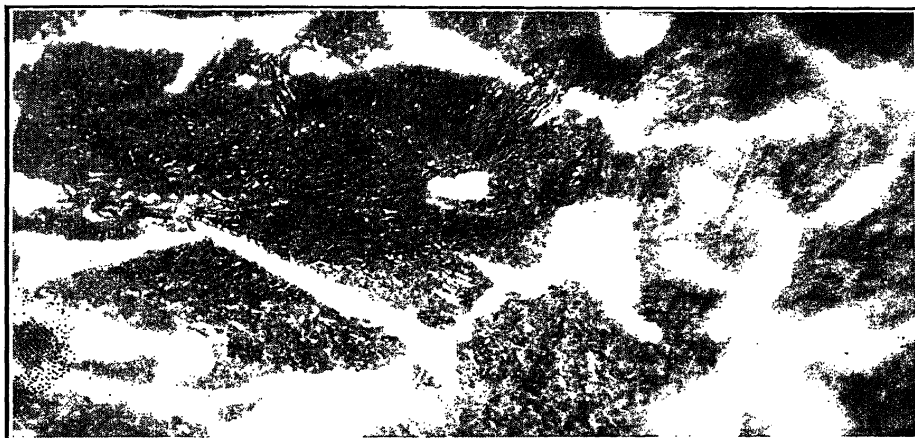
FIGURE 267.—Photo-micrograph of high-carbon steel, suitably polished and etched, magnified by 950. The white areas are cementite; the banded ones are pearlite.

516.5; shapes, 2374.3; plates, 2352.2; bars, 3897.1; concrete bars, 757.1; black plate for tinning, 2250.7; galvanized sheets, 1189.7; all other sheets, 5449.0; strip steel, 2854; pipe and tubing, 2946; wire products, 2717.8; all other finished steel, 1161.2; total finished steel, 29,622.6 thousand long tons.

[12] A collection of 56 photo-micrographs will be found in Vol. I of "The metallurgy of steel." F. W. Harboard and J. M. Hall. London. Chas. Griffin & Co., Ltd., 1923.

In ordinary steels the impurities also affect the properties; manganese makes the steel more elastic, hence more resistant to a shearing force. Chromium or tungsten raise the tensile strength; and chromium steel resists shocks beter than mere carbon steel.

Extra-hard steel may contain carbon only, or manganese 0.5 to 2 per cent with carbon 0.5 per cent and less; or 1 per cent tungsten with 0.5 per cent carbon; or chromium 1 per cent again with carbon 0.5 per cent.

Gun barrels [13] are made of chrome steel (1 or 2 per cent) (U. S.); armor plate for battleships (12 in. thick) is nickel-chrome steel (3.3 per cent Ni, 1 per cent Cr), case-hardened. Nickel steel (with 25 per cent Ni) is made in crucibles; the melted steel and melted nickel are poured together into a larger receiver. Nickel raises the tenacity without changing the elastic limit; vanadium has the same effect as nickel and only one-fifth as much is needed. A nickel steel with 3 per cent Ni, 0.40 C, 0.1 Si, 0.60 Mn, deoxidized by aluminum, possesses after heat treatment a tensile strength of 300,000 pounds per square inch; it is ductile and tough. Zirconium, molybdenum, and other elements are also used to strengthen steel.

Self-hardening tool steel, one of the most striking as well as important discoveries,[14] contains chromium 2 per cent, tungsten 8.5 per cent, carbon 1.85 per cent, manganese 0.15 per cent, silicon 0.15 per cent, phosphorus 0.025 per cent and sulfur 0.030 per cent. It is heated to 940° C., then cooled in a bath of molten lead, and after that, in the air; it is used for cutting tools in the machine shops, and retains its edge even though red hot from the friction of the cutting.

Columbium in Stainless Steels. Several iron alloys are briefly discussed in Chapter 45, among them stainless steels, which are precious to the chemical engineer because they resist corrosion. When stainless steels are subjected to heat, they become susceptible to corrosive chemicals. A way to preserve the non-corrosive property of the stainless steel consists in adding columbium (F. M. Becket); the columbium [14a] combines with the carbon in the steel, and the resulting carbide remains dissolved in the ferrite, in the straight chromium stainless steels, or in the metal, for such alloys as 18–8. The difficulty is thought to have been that chromium carbide formed a carbide which segregated. The amount of columbium added, in the form of ferro-columbium, is about five times its carbon content; to be effective, the carbon content must not be over 0.02 per cent.

Heat Treating. Every steel has a critical point, which is different for each one; for example, the critical point for .20 per cent carbon steel is 1560° F. (849° C.), while for 1.00 per cent carbon steel, it is 1375° F. (746° C.). When the steel is heated beyond its critical temperature, a change in properties takes place.

[13] A 14-inch (bore) gun consists of gun proper, inner tube, jacket, hoops and breechlock pieces; it requires about 2 years to manufacture; it is about 40 feet long. The smaller guns up to 3 inches have tube, inner tube, jacket, and breech-lock. The jacket is forced while hot over the tube (shrunk on).

[14] By Taylor and White, of the Bethlehem Steel Co.

[14a] For source and method of extraction *see* Chapter 49.

The various types of heat treating are: 1. Annealing, which means heating above the critical point and holding it there for 24 to 72 hours, then cooling slowly while covered. 2. Normalizing, which is the same as annealing, except that the steel is allowed to cool in air, which is also faster. 3. Quenching or hardening; that is, plunging the steel heated to above its critical point, into a 10 per cent salt solution, or into water, for rapid cooling; or into oil, for medium rapid cooling. Some steels having a high alloy content can be cooled in air. The process of quenching preserves the structure as it is at the high temperature; it produces a high degree of hardness. 4. Tempering, or better, "drawing," which means heating the hardened (quenched) steel to a certain temperature which must not in any case equal or exceed the critical point, and holding it there for some time. Drawing moderates the great hardness produced by quenching, and restores some of the original ductility. Example: A .45 per cent carbon steel quenched in water has 600 Brinell hardness; it is heated at 800° F. (427° C.) for one hour per each inch of thickness. The resulting steel has a 444 Brinell hardness. For ordinary work, these drawing temperatures range from 500° F. to 1200° F. (260° to 649° C.).

Several classes of carbon steels, which make up 85 to 90 per cent of heat treated steels, are distinguished, and their susceptibilities to heat treatment differ. Steel with carbon from .03 to .10 per cent (3 point to 10 point) is used for sheets, chain steel, angle iron, and is not heat treated; neither is the next class, .10 to .30 per cent carbon steels, which comprise structural steel and steel which will be case-hardened. Steel with .30 to .60 per cent carbon is the forging grade; it is made into automobile crankshafts, wrenches, and it is heat treated. (Generally, steel with carbon over .40 is for heat treating purposes.) The next class, .60 to .80 per cent carbon steels are for dies, chisels, punches and rails, and is not heat treated; while the following one, .90 to 1.05 per cent carbon, for automobile springs, is oil quenched and heat treated. File steel is 1.15 to 1.30 per cent carbon and is extremely hard.

Case-Hardening. In order to harden the surface while the interior remains soft and tough, steel may be enclosed in a thin case of carbon-rich metal, by heating it while packed in carbonaceous materials. Powdered bone, wood charcoal, charred leather, graphite, anthracite, lampblack, potassium cyanide (fused), sodium cyanide (fused), potassium ferrocyanide, acetylene, propane and other substances are used. The heating is out of contact with the air. The carbon of the packing slowly penetrates into the steel (nickel-steel automobile gears are case-hardened to a depth of 0.040 inch); the steel is usually cooled to a black heat, reheated to a high temperature, and then quenched, in order to temper the case. Balls for bearings are case-hardened, also cams, knives for weighing scales, gears of all kinds, rifle barrels and many other objects. 98 per cent of case-hardened steels are treated as just described.

Nitriding.[15] "Within recent years, a new method of case-hardening

[15] Reviewed by Dr. Victor O. Homerberg, Massachusetts Institute of Technology, Cambridge, Mass., and Technical Director, The Nitralloy Corp., 230 Park Ave., New York, N. Y.

has been introduced. Briefly, it consists in subjecting the articles that have been made from special alloy steels to the action of ammonia gas whereby a very high surface hardness is obtained with very little or no distortion. This surface hardness is retained at elevated temperatures and the treated articles are markedly resistant to atmospheric, water, and to a considerable degree, salt water corrosion.

"Nitriding was originally introduced by Dr. Fry of the Krupp Works in Germany and has been further studied by metallurgists throughout the world, especially in France, England, and the United States.

"The steels that are used contain variable amounts of carbon together with approximately 1 per cent each of aluminum and chromium and 0.2 per cent of molybdenum or about 1 to 1.5 per cent of aluminum and 0.75 per cent of molybdenum but without chromium.
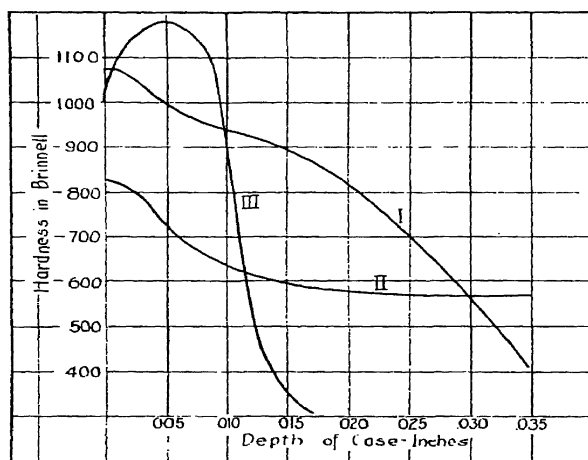
FIGURE 268. — Comparing nitrided steel and carburized steel. I, Cr-Al-Mo steel, nitrided; II, Ni-Mo steel, carburized; III, Cr-Mo steel, nitrided. (From *Metals and Alloys*.)

"The articles should possess a sorbitic structure before nitriding. As a general rule they are made from material that has been previously heat-treated. The nitriding operation is conducted by exposing the articles in an air-tight container to the action of ammonia gas, the flow of which is controlled by a suitable needle valve. The ammonia dissociates to some extent into atomic nitrogen and hydrogen in accordance with the following reaction: $2NH_3 = 2N + 3H_2$. The amount of dissociation is controlled by regulating the flow of the gas. Generally a dissociation of 30 per cent is desirable. The articles, after being exposed to the gas for the required length of time, are cooled in the container to room temperature, as a rule, and no subsequent heat-treatment is given to them. The atomic nitrogen reacts principally with the alloying elements to form nitrides. The cause of the great surface hardness is due, very likely, to the formation of a supersaturated solution of these nitrides

in iron followed by their partial precipitation in a manner to produce critical dispersion.

"The container for the nitriding operation should be constructed of materials unaffected by nitrogen or hydrogen. There have been suggested among others: steel with 25 per cent Cr and 20 per cent Ni; enameled iron, nickel, or monel metal and Inconel.

"The hardness, which gradually decreases from the surface of the core, corresponds to a Vickers Brinell value of 950 to 1200. The hardness of the surface of an article case-hardened by the ordinary process corrsponds to about 800 to 900 Vickers Brinell.

"In Figure 268 the hardness and depth of case for three case-hardened steels are shown.[16] Curves I and III are for steels of the composition shown below; Curve II is a nickel-molybdenum steel (S.A.E. 4615), which was carburized 8 hours at 1650° F. (900° C.), hardened by a double quench, and tempered at 300° F. (149° C.). The steel marked I was nitrided 90 hours at 975° F. (524° C.); steel III is also a nitrided product.

	I	III
C	0.30–0.40	0.18
Al	0.60–1.20	...
Cr	0.80–1.30	3.00
Mo	0.15–0.25	0.40
Fe	balance	balance

"The commercial development of the Fry process in the United States is controlled by the Nitralloy Corporation. Besides nitriding steels (Nitralloy) a cast iron, which can be nitrided, is on the market. This cast iron is known to the trade as Nitricastiron. Nitricastiron is being cast centrifugally with great success, but as yet, all of the variable factors involved in sand casting the material are not under complete control, although marked progress is being made in this direction.

"Nitriding at the present time is somewhat more expensive than case-hardening by carburizing. The use of ammonia in large quantities with a consequent marked reduction in its price together with the use of semi-continuous or continuous furnaces will lower the nitriding cost to a considerable degree. The many valuable properties of nitrided Nitralloy make this material of great value for many applications where resistance to wear is an important factor."

CRUCIBLE STEEL, ELECTRIC FURNACE STEEL

In the cementation process, iron bars of high purity were packed in charcoal, enclosed in a box, and heated for periods of many days. After cooling (also several days), the bars were unpacked and worked in variety of mechanical ways in order to make them homogeneous. The product was a high carbon steel, at that time the hardest (after suitable tempering) steel available. This lengthy process was superseded by the

[16] "Nitriding for the engineer," O. E. Harder, *Metals and Alloys*, 330 W. 42 St., New York, N. Y., **2**, 132 (1931).

crucible process, in which a steel of uniform composition could be made in less time. Melting the steel offered the additional advantage that additions other than carbon could be made, such as other metals, which had the property of hardening steel. The crucibles have in turn been displaced by the electric furnace, which may be considered rather a large
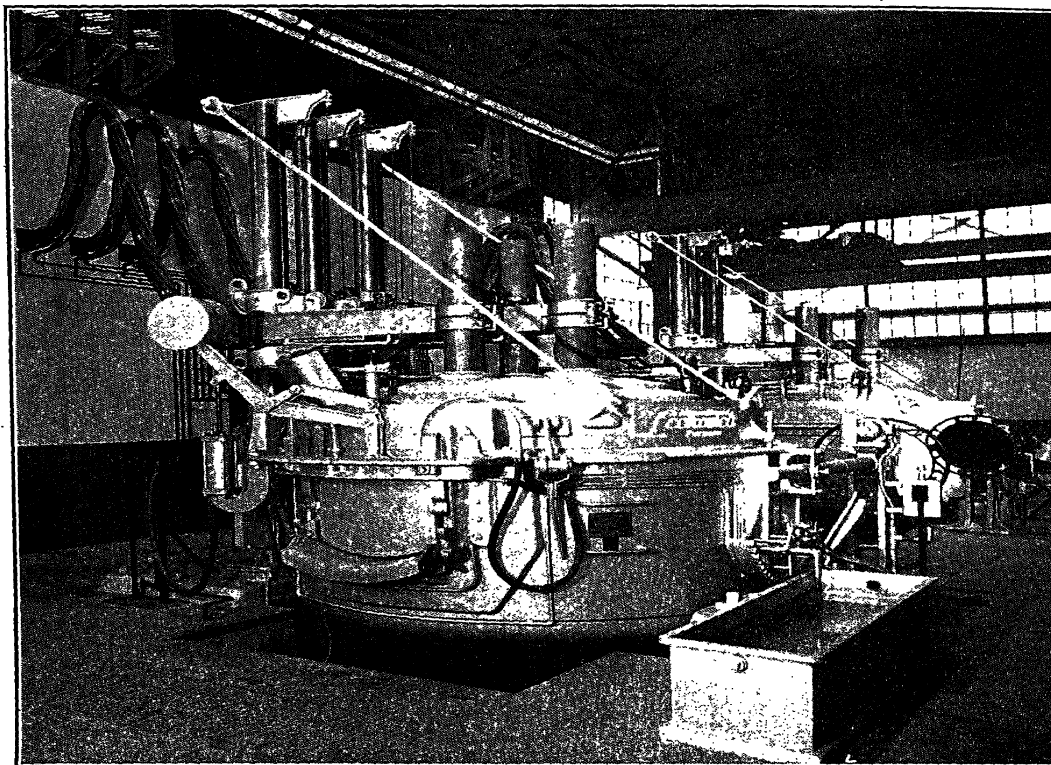
FIGURE 269.—Two 'Lectromelt furnaces, each of three-ton per hour capacity, of the top charge type. When the charge is finished and ready to pour, the furnace is tilted, and the metal run into ladles. The furnace is righted, the electrodes are lifted, anchoring bolts opened, and the top of the furnace rotated to the left of the reader, exposing the whole of the interior, for easy charging of the next batch. (Furnished by the Pittsburgh Lectromelt Furnace Corporation, Pittsburgh.)

crucible in which heat is applied directly to the charge, by the conversion of electrical energy to heat, and need not pass through the walls of the crucible.[17]

The capacity of the steel furnace is not large; it runs from 1200 pounds to as much as 6000 pounds (tool steel) at one pour. A coreless induction

[17] The Stassano, Keller, Girod, and Heroult furnaces are discussed in *Electrochem. Met. Ind.*, 7, 255 (1909), with illustrations. *See also* Chapter 4 on the steel furnace, in "The steel foundry," J. F. Hall, New York, McGraw-Hill Book Co., 1922.

furnace has been found well adapted to melting cobalt high-speed steel, tungsten high-speed steel, heat-resisting alloys, corrosion-resisting alloy and special compositions for tool and magnet steel. A number of special alloys are listed in Chapter 45.

The materials charged are selected scrap, flux, deoxidizers, muck bar (a very pure steel), ferro-tungsten, for example, and other alloys.

It is essential to make a distinction between structural steel and crucible steel; the former is made in huge quantities, and sells under 10 cents a pound, while the latter is made in small lots, and brings 80 cents a pound.

Ferro-Alloys. A number of ferro-alloys are made in considerable quantities. Ferro-manganese and its lower grade, spiegeleisen, are made in the blast furnace from manganese-bearing ores. The stronger grades of ferrosilicon, perhaps the most important ferro-alloy, are made in the electric furnace; ferrochrome, ferrotungsten, and ferromolybdenum also. The lower grades of ferrosilicon, up to 10 per cent, are made in the blast furnace, by increasing the coke ratio. Ferrovanadium is made by the thermite (Goldschmidt) process; ferrotitanium is made to some extent by the thermite process, but partly in the electric furnace.[18]

There was produced a total of 592,176 gross tons of ferro-alloys (15 varieties) in 1935, with a value of $48,891,592.

Comparison. The relative importance of the Bessemer, open-hearth and other processes for steel is shown in Table 80.

TABLE 80.—*Production of Steel in the United States, by Process. (Long Tons.)*
(Bureau of the Census.)

	1935	1934	1933
Open hearth basic	30,418,913	23,256,417	20,033,695
Open hearth acid	438,985	274,688	304,089
Bessemer	2,839,397	2,162,357	2,428,585
Electric	707,515	361,825	396,344
Total	34,404,809	26,055,289	23,162,713

All the Bessemer steel in this table is acid Bessemer, and most of the open-hearth is basic open-hearth; the latter is gaining in tonnage at the expense mainly of the Bessemer.

The price for finished steel, a composite, for 1936 was $2.41 per 100 pounds. Steel billets for re-rolling, essentially open hearth steel ingots in a more convenient form, averaged $30 per long ton in 1936.

OTHER PATENT

U. S. Patent 1,786,322, electric furnace for melting metal.

PROBLEMS

1. A charge of metal for a basic open hearth furnace weighs 225,000 pounds and contains 1.4 per cent silicon; the metal tapped weighs 200,000 pounds and contains 0.004 per cent Si. All the silicon has formed calcium silicate $CaSiO_3$. How much calcium silicate is obtained?

[18] "The ferro-alloys," J. W. Richards, *Ind. Eng. Chem.*, 10, 851 (1918). An up-to-date discussion of ferro-alloys will be found in the chapter on "Metals and Ferro-alloys used in the manufacture of Steel," by W. J. Priestley, pp. 615-621, in "Metals Handbook," 1936 ed., Cleveland, O.

The corresponding figures for phosphorus are 0.1 per cent in the charge and 0.02 per cent in the metal; calcium phosphate is formed, $Ca_3(PO_4)_2$. How much? In the acid open hearth, no lime is added; the silica forms iron silicate with the iron oxide, FeO; using the figures given above for silicon, and assuming enough ferrous oxide to be formed, how many pounds of iron silicate would be formed?

2. A 10-ton charge in a Bessemer converter has the composition given below: C 3.50 per cent; Si 2.10; P 0.04; S 0.044; Mn 0.48. Right after the blow, before any addition is made, the steel contains no carbon, no silicon, no manganese, while the phosphorus and sulfur content are unchanged. From the heats of combustion below, compute the number of Btu. evolved; and comparing Chapter 12, find the weight of coal which would be equivalent to this amount of heat.

1 pound of silicon	on burning to SiO_2	evolves 12.700 Btu.
1 " " phosphorus " " " P_2O_5		" 10,700 "
1 " " manganese " " " MnO		" 3.000 "
1 " " carbon " " " CO		" 4,409 "

NOTE: For other problems consult "Metallurgical calculations," in 2 vols., by Joseph W. Richards, New York, McGraw-Hill Book Co., 1910; steel problems are in vol. 2.

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The iron-carbon-temperature diagram will be found on p. 140, in "The Phase Rule," Alexander Findlay, London and New York, Longmans, Green and Co., 1927, or on p. 253 in the "Metals Handbook" for 1936, or on p. 438 in "The metallography and heat treatment of iron and steel," Albert Sauveur, Cambridge, Mass., Sauveur and Boylston, 1916.

"Metals Handbook," 1936 edition, American Society for Metals, 7016 Euclid Avenue, Cleveland, Ohio.

The study of metals involves the application of several sciences. The extraction of the metals from their ores, and the finding of the ores, is the task of metallurgy. In explaining the origin of the ores, metallurgy leans on geology; in choosing the reactions for the extraction and refining of the metals, the metallurgist applies chemical science. An important branch of metallurgy is metallography, the study of the internal structure of metals and alloys.

Chapter 49
Copper,* Lead, Zinc, Tin, Mercury

The metals copper, lead, zinc, tin, and mercury form a middle group of metals, more expensive than steel and iron, but cheaper than the precious metals. They may be described as base metals, because they are relatively easy of attack by acids and reagents, and because they form the oxide when heated in a blast of air. The precious metals remain unaffected under such conditions; in fact, silver is rid of lead by oxidizing the latter. The relative importance of copper, zinc, and lead is shown by the table below,[1] which also indicates what portion of the metals are produced in the United States. Mercury is less important and will be treated separately; nickel and tin are discussed further on:

TABLE 81.—*Production of Copper, Zinc and Lead.*

		United States production — Tons	World production
Copper	1929	1,024,213	2,118,209
	1932	254,877	986,973
	1935	379,353	1,603,132
	1936	602,875	
Lead	1929	624,154	1,753,179
	1932	251,689	1,178,556
	1935	336,764	1,420,381
	1936	368,355	
Zinc	1929	572,988	1,472,788
	1932	193,715	789,949
	1935	391,456	1,349,350
	1936	576,175	

It will be noted that for each metal, a considerable part comes from the United States; the proportion is likely to remain the same in the future except for copper, which may be produced extensively in Africa. The production of mercury is decreasing in the United States, while the Italian and Spanish productions are increasing. The nickel refined in the United States is chiefly from Canadian ores, while the tin is from ore shipped in from the Malay Peninsula.

Compared with pig iron, these productions are small, but the uses of

* With advice from Mr. H. R. Tumin, Min. E. (Carnegie Tech.), of Buffalo, N. Y.
[1] Data in this and other tables in this chapter from "The mineral industry in 1930," by G. A. Roush, New York, McGraw-Hill Book Co., 1931.

these metals are so specific that it would be difficult to do without them. It is interesting to note that copper serves to transmit [2] the electrical current, and to collect it at the generator; zinc serves in dry cells; while lead is the metal used in storage batteries; hence all three are closely connected with electrical practice. Other uses of the metals and their alloys will be found at the end of the chapter.

COPPER

Copper, the red metal, occurs in the native form only in the Upper Peninsula of Michigan; the shafts are deep (5000 and 6000 feet). A number of blocks of the metal have been found which are so large that they cannot be brought to the surface through the shaft; and they cannot be dynamited to smaller fragments because the metal is soft enough to yield, preventing fracture. Other copper fields have combined copper, mainly as sulfides, but also as carbonates and silicates. Examples are chalcopyrite, $Cu_2S.Fe_2S_3$; bornite (peacock ore), $3Cu_2S.Fe_2S_3$, richer in copper (55 per cent); chalcacite, Cu_2S, with 80 per cent copper; azurite, and malachite,[3] $CuCO_3.Cu(OH)_2$, carbonates; chrysocolla, a silicate. Malachite is of an intense green color; azurite and chrysocolla are blue. When the ore occurs in veins, a high-grade material is obtained, with 8 to 12 per cent Cu; but low-grade ores are also profitably mined and worked to as low a content as 1 per cent. The principal producing countries are indicated in the table below:

TABLE 82.—*Copper Production*

	1929	1932	1935
		Metric tons	
United States	931,103	231,798	344,867
Africa	156,547	140,783	268,519
Chile	316,813	103,173	267,336
Canada	109,908	113,736	188,901
Japan	75,469	61,780	66,000
U. S. S. R.	25,803	30,678	63,000
Mexico	78,708	34,100	41,622
Spain-Portugal	48,625	29,609	31,623
World	1,921,639	895,382	1,454,357

Within the United States, the production in the several States and territories would allow the following order, for tonnage produced: Arizona, Utah, Montana, Nevada, Michigan, Alaska, Colorado, California, New Mexico, and others. The Montana ores (Anaconda) are high-grade sulfides; in the Miami district in Arizona, the ores are low-grade sulfides. Nevada (Ajo) has azurite and malachite, and the mines are of the open pit type. The Arizona copper mines are shaft mines and in fewer cases, open pit type (Jerome); Bingham in Utah is an open pit mine.

Concentration of the Ore. The high-grade sulfide ore, with 2 to 8 per cent copper, is concentrated by floating off the lighter earth and rock with flowing water, in classifiers such as the Dorr, in jigs, or on

[2] Aluminum is well suited for power transmission.
[3] The Egyptians used malachite for carvings.

shaking tables with grooves; the jigs are the older devices and are being displaced by the classifiers. A preliminary crushing gives the desired size. For low-grade ores, the crushing in jaw crusher [4] or gyratories [4] is followed by pulverizing in ball mills [4] to pass (90 per cent) through a 40-mesh screen. After screening, the fine material sometimes receives the "coating oil", with which it is intimately mixed; the oiled powder next passes to the flotation machines, with either paddle or air agitation. More generally, the ore receives no preliminary oil treatment. The flotation machine contains the "frothing oil" suspended in water; the emulsion so formed has a selective action on the crushed ore; the sulfides are lifted into the froth, while the worthless material sinks. The lifting is done by a bubble of air which adheres to the oil-moistened particle and carries it up. The froth overflows to rotary suction filters which deliver a cake of concentrated ore, dry enough to be sent to the smelter. The flotation machine is small, and batteries consisting of many units are used.

The oil which serves for flotation is usually creosote oil. In amount it is surprisingly small, perhaps one quart to a ton of ore. Besides the creosote oil, pine oil, certain coal-tar oils, kerosene acid sludge from the refineries, and a few others, are suitable. Mineral salts and organic substances are also added, with the oil.

Without the flotation system, it is doubtful if low-grade ores could be profitably extracted.

Smelting of the Concentrated Sulfide Ore to Crude Copper. The concentrated ore is placed on the hearth of a reverberatory furnace [5] and heated with free access of air. Sometimes the ore is first melted and cast into pigs, and these fed to the furnace. As the melting progresses, a part of the sulfide becomes oxidized, and the oxide acts on unchanged sulfide, liberating the metal and forming sulfur dioxide gas. The mass has melted by this time, and the metal sinks to the hearth; it is tapped at intervals. A flux is added in order to bind siliceous admixtures, and the slag which forms lies at the surface. The reaction between the oxide and the sulfide is violent and audible:

$$Cu_2S + 2Cu_2O = 6Cu + SO_2.$$
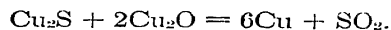
The product of this operation is crude copper, called blister copper, because it has cavities due to escaping gases. The blister copper is cast into anode sheets for the electrolytic refining. Blister copper is about 98 per cent Cu; it retains any gold or silver which the ore contained.

There is another way to make crude or blister copper, consisting of two steps. First the ore is charged into the rectangular blast furnace (24 or 30 feet long, 4 feet wide) with coke and flux, and there melted; the copper sulfide remains sulfide, but the gangue is removed as a slag, so that the result is really a purification of the copper sulfide now called the "matte". It is tapped at intervals, and used while still hot in the

[4] Chapter 44.
[5] Chapter 4.

next step, the Bessemer converter. The slag is also tapped at a special taphole.

The hot melted sulfide is fed to a small converter (1 to 3 tons) resembling the Bessemer for steel [6] with, however, an important difference: the tuyeres are in the side of the converter, high enough so that the metal formed drops below them and escapes the oxidizing action of the blast. A small amount of acid flux is added, and the blowing performed. Sulfur dioxide escapes, and the metal sinks below the tuyeres; as the heat evolved is not so high as in the steel converter, the metal is less fluid, and this construction prevents the choking of the tuyeres. The converter is discharged by tipping. The iron impurities are oxidized and form silicates with the acid lining of the converter, or with the flux.

The tendency is to combine the two steps, blast furnace followed by the converter, into one, by melting in the converter itself (horizontal cylinder) and then blowing the melted sulfide.

Certain ores are adapted for treatment by the two-stage pyritic method, in which a saving of fuel is effected by using the heat of combustion of the iron pyrite which they must contain; a copper matte is produced which is made into blister copper in one of the ways described above.

There are many variations in the smelting of copper sulfide ores; in many cases a preliminary burning off of much of the sulfur, called roasting, is a separate process. It is performed in rotary shelf burners, similar to the Herreshoff furnace described in Chapter 1; or in the Dwight-Lloyd sintering machine, in which an endless belt made of cast-iron buckets with perforated bottoms pass over a strong suction box after their ore contents have been ignited by an oil flame.

Wet Methods of Extraction. The methods just given apply to sulfide ores only. Azurite and malachite may be extracted by the sulfuric acid-leaching process; a solution of copper sulfate results from which the copper is precipitated partly by electrolysis, the rest in powder form by old iron (Ajo district in Nevada). This might be called the acid-leaching method.

The ore (1.3 to 2 per cent Cu) is dumped into tanks 88 feet square, 17 feet deep, made of reinforced concrete, with wooden bottoms, and leached 8 days on the countercurrent principle. The copper sulfate liquor with 2.985 per cent Cu is passed into the electrolytic deposition cells, with (impassive) lead anodes, and copper sheet cathodes, on which latter the liquor deposits a part of its copper; the outgoing liquor with 2.513 per cent Cu and a gain in sulfuric acid is strengthened by further leaching and reaches the cells again; this is continued until the impurities have accumulated so much that the liquor must be discarded. The remaining copper is then precipitated by scrap iron.[7]

[6] Chapter 48.

[7] "First year of leaching by the New Cornelia Copper Co.," Henry A. Tobelmann and James A. Potter, *Am. Inst. Mining Eng. Bull.*, **No. 146**, 449 (1919). *Compare* also the article by William E. Greenawalt, "The Greenawalt electrolytic copper extraction process," *Am. Inst. Mining Met. Eng.*, **70**, 529 (1924).

In the early days of copper mining in Michigan, the tailings, still containing an appreciable percentage of copper, were washed into the lake from the stamp mills; now that the mine shafts must be deeper than formerly, operation costs have risen and it has become profitable to work over the discard of former days. This is done in part by concentrating by means of classifiers and shaking tables, the remainder by leaching with an ammonium carbonate solution.[s] Acid leaching would not do, for the gangue is mainly calcite, which would consume the acid.

The old discard from the stamp mills, with 0.8 per cent Cu, is brought up from the lake bottom by sucker dredges, screened twice, and classified. The Dorr classifier, for example, is of the drag type. It consists
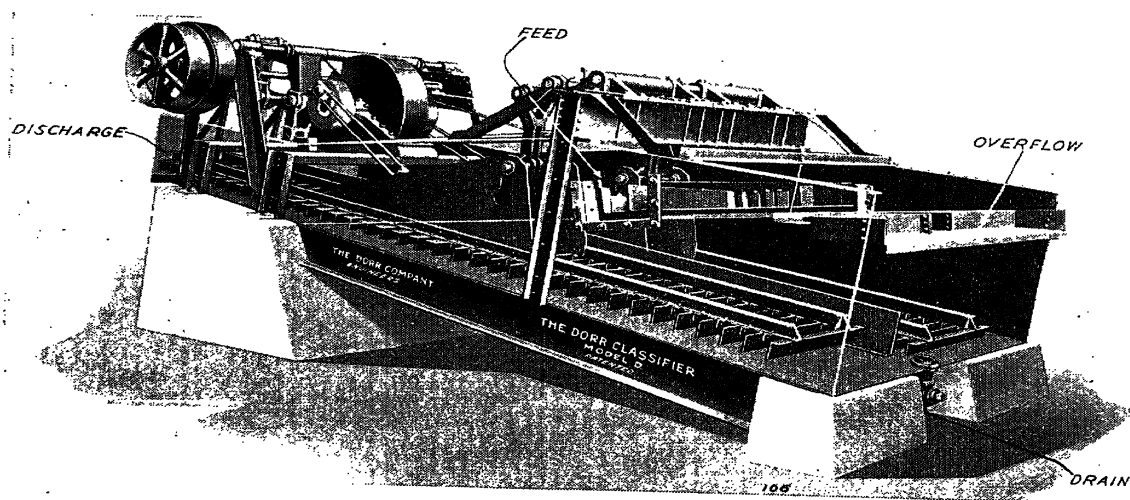
FIGURE 270.—The Dorr classifier, with inclined trough, rakes which sweep up, then are lifted out by a cam for the return stroke. (Courtesy of the Dorr Co., Inc., New York.)

of an inclined trough in which scraper blades move in the sand toward the upper end, returning to their first position while raised and outside the sand. A stream of water carries down the lighter particles which the blades dislodge, while the heavier particles are pushed up along the floor and are finally discharged at the upper end. This upper discharge called the "sands" and richer in metal now, is ground in a Hardinge[9] mill, concentrated, and the concentrated portion sent to the smelting furnace. The weak tailings after suitable classification and concentration reach the leaching tanks. These are steel tanks 54 feet in diameter, 12 feet high, provided with covers; the contents of such a tank are percolated with the ammonium carbonate solution for 72 hours. At the

[s] "Ammonia leaching of Calumet and Hecla tailings," C. H. Benedict and H. C. Kenny, *Am. Inst. Mining Met. Eng.*, **70**, 595 (1924).
[9] Chapter 44.

end, the copper solution is evaporated in tank-like stills, the ammonia recovered and used again, while the copper is left behind in the form of oxide. The residue in the leaching tank is washed and returned to the lake.

The chemical action is as follows: Cupric ammonium carbonate with excess ammonium carbonate dissolves native copper in the old discard, to form cuprous ammonium carbonate. This latter solution is the one which is distilled. The solution of cupric ammonium carbonate required for the extracting solution is obtained by treating a portion of the cuprous ammonium carbonate solution with air.

Still another wet extraction method which deserves brief mention is the one practiced at Rio Tinto, in Spain. The iron pyrite mined there contains 3 per cent copper. It is extracted by oxidation of the copper glance, Cu_2S, and washing out the copper sulfate formed. The ore is piled in heaps 30 feet high containing 100,000 tons; draft pipes are built into the heap, and the top has grooves and basins for the distribution of water. The wash water is passed over pig iron, which precipitates the copper metal. One-half the copper in the ore is washed out in 3 months, 80 per cent of the other half in 2 years. The ore is called washed when the copper content has been reduced to 0.3 per cent. The oxidation of the copper sulfide is due to the action of air and of ferric sulfate.

Electrolytic Refining of the Crude or Blister Copper. The crude copper with 98 per cent Cu is made into pure copper by electrolysis in a solution of copper sulfate kept slightly acid by sulfuric acid additions. For many years, the native lake copper was quoted one-eighth cent higher than electrolytic; lake copper is very pure, and very small amounts of impurities affect the properties of the metal to a considerable extent; it is now generally recognized that electrolytic copper made from sulfide and other ores is the equal of native or lake copper. The blister copper is cast into anodes, flat sheets 3 feet long by $3\frac{1}{2}$ feet wide, and three-quarters of an inch thick; these are suspended at a distance of 2 inches from the cathode, a copper sheet of similar dimensions except that it is as thin as paper (0.01 inch). The direct current passes through the solution; the anode decreases in thickness, while the cathode gains. During the transfer of the metal, the impurities are removed in various ways. The noble metals, silver and gold, drop off as the copper disintegrates, and deposit as the anode mud, worked up later into the precious metals. Nickel, cobalt, iron and zinc dissolve and remain in the solution; lead and bismuth form a sulfate mud; arsenic forms an insoluble arsenate with copper, and also drops into the mud. Every time an anode is replaced, the muddy liquid is pumped out.

By maintaining the proper voltage, none of the impurities plate out with the copper, hence its purity. The current density is 15 amperes per square foot of surface, the voltage 0.3 to 0.35 per plate, and the temperature 130° F. The electrolyte is circulated and periodically changed in order to remove the gradually accumulating soluble non-copper salts.

To further smooth deposition of the copper, 4 ounces of glue are added to every 12,000 cubic feet of electrolyte.

The cathode plates are remelted and cast into ingots.

LEAD

The important lead ore is galena, the sulfide, PbS, a black ore which is sometimes found well crystallized; its purity varies in the different deposits. Lead is also obtained from a mixed lead and zinc sulfide, and this in addition may contain silver. The production for the different countries is given in Table 83.

TABLE 83.—*Lead Production of the World; Smelter Production.*

	1929	1932	1935
		Metric tons	
United States	624,154	251,689	336,764
Australia	177,268	189,221	220,491
Mexico	248,783	130,293	185,225
Canada	144,392	117,676	150,012
Germany	97,900	95,200	122,300
Spain	123,261	109,769	70,823
Belgium	62,213	61,548	68,000
Total	1,753,179	1,178,556	1,420,381

In the production of lead, the United States leads; for the several States, the figures are as listed in Table 84.

TABLE 84.—*Mine Production of Lead in the United States, in Tons.*

	1930	1932	1935
Southeastern Missouri	198,622	116,152	96,941
Idaho	134,058	72,118	79,036
Utah	115,495	62,776	63,507
Tri-State Joplin district	36,972	18,131	36,100
Montana	10,653	1,079	15,612
Nevada	11,529	440	12,652
New Mexico	10,378	10,114	7,289
Colorado	22,130	2,150	5,673
Total	558,313	292,968	331,720

Two-thirds of the Missouri production of lead is from the southeastern portion of the State, where galena is found; the other third is from the southwestern part of the State, an area rich in zinc blende and lead-zinc sulfides; the main product in this area is zinc. The southwestern district is described in more detail under zinc, in the next division. Near Leadville, Colorado, the ores mined are mainly lead-zinc sulfides, carrying silver.

The method of extraction for galena ores includes a crushing and screening followed by classifying in a Dorr classifier or a similar device. The classifier delivers at one end the "sands", at the other, the "slimes". The sands are concentrated further on shaking tables, which yield concentrated ore, ready for smelting, and tailings which are treated further after pulverizing in a ball mill. The concentrated ore may be **60 to 70** per cent Pb, from an original ore 6 to 8 per cent Pb.

The slimes are thickened in a Dorr thickener and filtered, yielding a cake containing 60 per cent Pb.

The concentrated ore is smelted in a square blast furnace not over 10 feet high, or on a hearth; an improved form of the latter is the Newnman hearth, much favored in Missouri.

A simpler hearth for lead smelting is a shallow cast-iron box in which ore, fuel, and flux are placed, while the blast is applied from the rear, downward. The hearth is similar to an ordinary blacksmith's forge. The metal reaches the bottom and is siphoned off. Fresh ore and fuel are spread on constantly, and the mass is rabbled by hand. In the Newnman hearth, the rabbling is mechanical; its size is 8 feet in length, 20 inches wide and 8 inches deep, and its capacity is over three tons of lead produced in 8 hours.[10]

In the blast furnace, the ore mixed with the flux, which may be iron oxide and lime, and with coke as fuel, is fed in. Lead in the liquid form collects at the base and retains any silver or gold which the ore contained. The lime displaces the lead in any lead silicate which might have formed, while the iron oxide binds the sulfur which fails to burn off as sulfur dioxide, as iron sulfide. The lead and slag are tapped at different levels, very much as is done with pig iron in the iron blast furnace. The iron oxide used in the charge is generally cinders from iron pyrite from the sulfuric acid plants.

When silver is absent, the first product is freed from antimony, tin, copper, zinc, sulfur, and iron, present in small amounts, by melting the lead and maintaining it at red heat in a reverberatory furnace. The impurities as oxides (except zinc) mixed with lead oxide (litharge, PbO) form a skin on the surface which is removed from time to time; to facilitate the removal, some lime is added, which stiffens the oxides. The zinc oxide passes off in the fumes.

If silver is present in small amounts, it is removed by melting the lead in one of series of pots and allowing it to cool slowly; the lead, free from silver or poorer in silver, separates as crystals which float at the surface, leaving the silver-containing lead, or richer lead, in the molten state. The crystals are ladled into the pot on the left, the melted lead into the pot on the right. The operation is repeated, until on the left lead free from silver is obtained, while on the right a lead rich in silver is collected. This process is known as the Pattinson process, which is used in Great Britain and on the Continent.

The silver-rich lead may be concentrated in another way, namely by adding melted zinc, which alloys with silver (gold at the very first, if any present) and forms a scum which contains the silver, leaving a melted lead poorer in silver. The separation of the silver is not complete, and must be repeated several times. The scum is distilled for zinc in graphite retorts, leaving lead and silver; this is treated for the recovery of the silver as described in the next chapter under silver.

[10] *Trans. Am. Inst. Mining Met. Eng.*, **54**, 485 (1917).

The zinc process is called the Parkes process and is the standard process in the United States. There is a variety in the details of treatment in the various plants, designed to suit the particular one treated.

The lead free from silver may now be purified in a reverberatory furnace, as described three paragraphs back.

A somewhat different procedure is the Harris process, in which crude melted lead is agitated with molten caustic (NaOH), which removes all the undesirable metals, including arsenic, but does not affect the silver. The purified lead is then desilverized.

A portion of the lead production, perhaps one-quarter of the total, is consumed in making white lead and other pigments.[11]

Quality of Ores. When copper is present in an ore forming part of mixture smelted in the lead blast furnace, the aim is to recover it in the form of matte (copper sulfide), which forms a middle layer, with the slag over it, the melted lead under. The matte forms only if enough sulfur is present.

Zinc is not recovered in the copper nor in the lead-smelting operations, but passes to the slag in part, and to the fumes. Over 10 per cent of zinc in the slag makes it viscous, decreasing furnace capacity; in the fumes, the zinc increases losses by volatilization. There is therefore a penalty of 30 to 50 cents for each per cent zinc above 1 per cent per ton. This heavy penalty has stimulated efforts to separate zinc blende from lead or copper before selling the ores to the smelter.[12] There is a bonus on iron because it fluxes out the silica without requiring the addition of purchased limestone. There is a penalty (light) for silica above a certain percentage.

ZINC

The zinc ores of industrial importance are the sulfide. ZnS, called zinc blende, and the carbonate, called calamine. The sulfide is white when pure, but the ore is generally brown or black from admixed iron or lead. The mixed sulfides of lead and zinc are also used, for both their metals. Zinc blende is more important than calamine. To these may be added franklinite, a double oxide of iron and zinc, and willemite,

TABLE 85.—*World Production of Zinc.*

	1929	1932	1935
		Metric tons	
United States	572,988	193,715	391,456
Belgium	197,900	96,330	182,660
Canada	78,064	78,157	135,266
Germany	102,000	41,981	124,200
Poland	169,032	84,950	84,994
Australia	50,804	53,655	67,909
Great Britain	59,235	27,308	61,433
France	91,611	49,330	51,464
World	1,474,788	789,949	1,349,350

[11] Chapter 31.
[12] *Bur. Mines Tech. Paper* **No. 83,** Ch. H. Fulton (1915).

a zinc silicate, both found at Franklin, New Jersey, and actively mined.

The output of spelter (zinc metal) in the several countries is given in Table 85; in a general way, the figures also indicate the production of zinc ore in the countries named.

It will be observed that the United States retains the lead in zinc production which it has in lead and copper; the two countries next in importance have not appeared in the list of copper producers, and only one, Belgium,[13] appears in the list of lead producers, in the seventh place. Within the United States the order is also quite different; in Table 86, the mine production of zinc ores, calculated to zinc metal, is stated.

TABLE 86.—*Mine Production of Zinc in the United States, in Tons.*

	1934	1935
Tri-State or Joplin district, Mo.		
Kansas	38,261	50,000
Oklahoma	107,772	134,000
S. W. Missouri	7.059	7,500
New Jersey	76,553	86.260
Montana	30.721	54.772
Utah	28.198	31.102
Idaho	24.799	31.098
New York	23.188	23.188
Total U. S. mine production	438,726	518,373

The mine production does not quite agree with the spelter production because there is a loss in smelting, and because ores are stored and worked up perhaps a year later. The tri-state district is placed together because, although part of three States, it is geologically a single deposit. Its area is only some 10 or 15 miles square; it lies in three contiguous counties, Ottawa (Oklahoma), Cherokee (Kansas), and Jasper (Missouri), of which Ottawa County is at the present time the best producer. Joplin lies in the district, in Jasper County. As the table shows, this district is the prime producer in the United States. The ore is mainly zinc blende.

After crushing, the ore is concentrated in jigs, shaking tables,[14] and by oil flotation; still another device sometimes used for zinc ores is the electrostatic separator (Huff). The concentrated ore is roasted in rotary shelf burners, which are the prototype of the rotary burner used for iron pyrite burning [15]; the sulfide is thus transformed into the oxide. The reduction of the oxide to the metal is performed in rather small, horizontal fireclay retorts, banked over each other, and set in a furnace receiving preheated gas and air; in this way, a high heat is applied to the retorts, and the metal formed within them is distilled into the fireclay receiver placed at the mouth of the retort. The volume of the retort is 1.5 to 1.9 cubic feet, which are filled with finely divided oxide mixed

[13] The main mine is the Moresnet, on the German border; it has yielded calamine, blende, and galena for many generations, and has been in continuous operation since the 15th Century (Vieille Montagne Company).

[14] Chapter 50.

[15] Chapter 1.

with 25 per cent non-caking coal. The receiver is capped by a third piece, the condenser, in which the first vapors of the metal condense as a dust (zinc dust); receiver and condenser have an opening through which the carbon monoxide formed passes out; it burns at the outlet from the condenser. The charge for a retort is 40 to 50 pounds of oxide. The metal for the main part collects as a liquid in the receiver, and is removed by a ladle. The number of retorts in the United States is 103,252 (1935), distributed in 20 plants, perhaps 60 to a furnace for the largest furnaces.

In the case of ores containing both zinc and lead, with the zinc above 10 per cent, the practice is to work the ore in the retorts for zinc, as described above. The residue is then handled as a lead ore would be. With the zinc below 10 per cent, the ore is worked for lead, and the zinc passes out as oxide in the fumes.

Electrolytic Zinc. Just after the war, electrolytic zinc was a curiosity; since then the demand has steadily increased. Of the United States production for 1935, 28 per cent is electrolytic zinc, 72 per cent is distilled zinc; outside the United States, 43 per cent of the production is electrolytic. Electrolytic zinc sells at 4 cents above the market for spelter, yet in spite of that, it is bought; the reason is that its high purity, 99.999 per cent, gives it superior properties, particularly corrosion-resisting qualities. Its high purity is primarily the result of the necessity of having the deposition bath absolutely pure, if any zinc is to be deposited at all.

The roasted ore is dissolved in the spent acid from the cells, iron added to remove arsenic and antimony, manganese dioxide (if not present in the ore) to oxidize the iron, zinc oxide to precipitate the iron, and zinc metal to remove copper, cobalt, and nickel. The resulting pure solution is then electrolyzed.

Indium Extraction. Indium occurs in many zinc ores, and may be isolated by using the following sequence of operations:[15a] the ore concentrate, mainly sulfides, is roasted (at 400 to 600° C. (752 to 1112° F.)) to produce a calcine, mainly oxides. The calcine is leached in a series of Pachuca tanks with sulfuric acid. The solution carries Zn, Fe, Au, Ag, As, Sb, and substantially all the indium. The acid solution receives calcium carbonate in the last tank, which causes the separation of In, some Fe, Au, Ag. Cu. This precipitate is now treated in other Pachucas with acids, with air agitation. The metals redissolve. The solution is now treated with zinc metal, so that In, Au, Ag, Cu separate in the metallic form. These solids are treated next with 25 per cent sulfuric acid for $1\frac{1}{2}$ hour, and the solution so obtained receives hydrogen sulfide, which throws out Au, Ag, and Cu as sulfide, but not the indium. The slurry is filter pressed, the filtrate blown free of hydrogen sulfide, and sent to the electrolytic tanks, where the indium is plated out, practically pure.

Moistening the ore concentrate with sulfuric acid, and roasting this wet

[15a] U. S. Patent 1,847,622; *see also* 1,839,800.

concentrate at 1100 to 1250° F. (593 to 677° C.) leads to increased yields of indium.[15b, 15c]

Another method provides for the recovery of indium (and gallium) from the lead-containing retort residues in the zinc distillation process.[15d]

TIN

Tin ore is obtained from river gravel, and is concentrated by washing essentially as for ores discussed in the preceding divisions. The total production of tin ore expressed as tin metal, for the world (1935) was 146,471 long tons, of which 45,919 tons originated in the Malay Peninsula and were shipped in part to Raritan, New Jersey, for extraction, while 27,168 tons of Bolivian origin were shipped to Great Britain. The metal is obtained by reducing the ore, which is generally the impure oxide, SnO_2, with coal on the hearth of a reverberatory furnace. The crude metal so obtained is refined by placing it, after solidification, in the furnace and heating gradually, so that the melting is slow; the first metal is the purest; this system is called liquation, and is used for some of the other metals also. A further refining is by melting the metal in a pot, and suspending in it poles of green wood; the gases formed agitate the metal, and the impurities oxidize, forming a scum which can be removed. Poling is used for other metals also.

MERCURY

The chief ore used for the extraction of mercury is the sulfide, HgS, cinnabar, a red ore. The chief United States producer has been California (the new Idria mine in San Benito County); the production for Spain for 1936 and 1937 will suffer from its unfortunate civil war.

TABLE 87.—*World Production of Mercury in Metric Tons.*

	1929	1932	1935
United States	817	435	595
Spain (Almaden)	2,476	816	1,227
Italy	1,998	1,016	878
Mexico	83	253	216
Total	5,610	2,850	3,330

The production for mercury is usually given in terms of flasks (made of cast iron) of 75 pounds each; as a result, such figures are larger, numerically, and likely to lead to an overestimation of the mercury production; in the table above, the usual ton (2000 pounds) has been used, so that comparison with any other metal in this chapter, and in the two preceding ones, may be made at a glance. Mercury is quite evidently of minor importance; its uses have diminished; mirrors are not made with its aid any more, and the amalgamation method of removing gold from the accompanying rock is giving place to the cyanide method.

[15b] U. S. Patent 1,912,590.
[15c] Silver-indium alloys are presented in Chapter 50.
[15d] U. S. Patent, 1,855,455; 1,886,825.

It is still used in countless ways of semi-scientific nature, but in amounts very small. A considerable use remains in dental fillings, and even this use will call for less new metal than formerly (at least in proportion) now that the mercury from the waste amalgam, reworked primarily for its silver, is recovered. Mercury is consumed for the manufacture of mercury fulminate, which has held its place for the explosives of war as well as peace explosives. Mercury as the working substance in boilers and turbines is presented in Chapter 12.

Cinnabar is roasted; the free metal and sulfur dioxide form. They pass together into a series of chambers where the velocity of the gas is reduced; the mercury deposits, while the sulfur dioxide passes out. The partly cooled gases may also be passed through small air-cooled glass condensers (aludels). The metal may be refined by distillation. Mercury alloys with many metals, to form "amalgams", but not with iron nor with platinum; the metal it attacks easiest is gold.

NICKEL

Almost no nickel is mined in the United States.[16] The world production in 1935 was 80,000 tons of nickel metal, of which 69,044 tons were produced in Canada. The production will undoubtedly continue to increase in coming years, especially if monel metal is included. The chief ore is pendlantite, a complex sulfide of iron, copper and nickel found in the Sudbury district, its nickel content is 3 to 3.5 per cent. Monel metal is discussed in chapter 45.

The deposits in New Caledonia in the South Pacific, the main source of nickel until the Sudbury basin was discovered, consist of an oxidized ore of the garnierite type.

At Copper Cliff (Sudbury) the mixed sulfides are ground fine, classified, roasted in Herreshoff burners to remove some of the sulfur, smelted in reverberatory furnaces and blown in Bessemers with addition of silica-bearing fluxes to remove most of the iron as a slag. The still impure mixed copper and nickel sulfide is then treated by a special process (Orford) in order to concentrate each. It is heated in a reverberatory furnace with sodium sulfate and some coal, so that sodium sulfide results. An essentially homogeneous melt results, which is run into medium-sized receptacles and allowed to cool slowly. There is formed at the bottom a hemispherical cake of nickel sulfide with still some copper sulfide, over it, a "tops" of copper sulfide with still some nickel sulfide, and throughout both, sodium sulfide. The bottoms are concentrated further by a second melting, and perhaps a third; similarly the tops. The separation is a physical process; the sodium sulfide serves as floating agent.

The bottoms with 74 per cent Ni and 1.5 per cent Cu are sent to Port Colborne, where they pass successively through a jaw crusher, a ball mill, a 10-mesh screen, to reach a rectangular lead lined tank with false bottom. In this tank, the ground material is leached with hot water to

[16] In 1935, 29,880 tons of nickel metal were imported, mainly from Canada.

remove sodium sulfide, then, with sulfuric acid to remove most of the remaining iron. The nickel sulfide, now with 76 per cent Ni and 24 per cent S, is divided, and treated further in two ways. One is by roasting on a Dwight-Lloyd sintering machine; the resulting oxide is mixed with 20 per cent coal and heated in an open hearth furnace to give the liquid metal, 96 per cent pure, (2 per cent Cu, 1 per cent Fe, S, Co) which is cast, when the furnace is tapped, into thick slabs weighing 490 lbs. These are purified by electrolysis.

The other way is by calcining in a one-hearth calcining oven, with rabbles which stir the ore and also move it at a slow rate toward the hot end, where an oil flame supplies an intense heat, in order to insure the removal of the last of the sulfur. The resulting nickel oxide goes in part to the Mond reducer, a shelf tower with rabbles, where it is reduced to nickel. In part, this metal serves in the purification of the electrolyte liquor, by precipitating an equivalent amount of copper. The black oxide is sold to a considerable extent to potteries for decorating tableware.

The Mond reducer works at 400° F. (204° C.), is 35 feet high and is built of cast iron sections, each having a heating chamber, surmounted by two shelves, one with central, the other with circumferential discharge. A central vertical shaft carries the arms and rabbles. The oxide moves down, as water gas passes upward; from the top, the not quite exhausted water gas is led back, and is burned to furnish the heat (supplemented if needed) to the heating chambers.

For the purification, the anode is suspended in a solution of nickel sulfate, and the metal driven across to the nickel starting sheet ($28'' \times 36''$), itself produced by depositing the nickel for 3 days, from the same bath, on aluminum, then stripping off the thin nickel sheet. The anode cycle is 41 days. The electrolytic tanks are concrete, $5' 2''$ deep, coated with gilsonite, with divisions accommodating 31 anodes and 30 starting sheets, each anode facing a starting sheet less than $2''$ away. The voltage is $2\frac{1}{2}$ volts; the current density 12 amperes per square foot. As the nickel anode dissolves, copper and iron enter the electrolyte; they are prevented from plating out by the continuous removal of the electrolyte to a purification system and the continuous infeed of purified electrolyte into a canvas box enclosing the cathode so that an electrostatic head can be maintained which prevents the foul solution from reaching the plate. The precious metals, on the other hand, remain as a mud on the last thickness of the anode; they are collected, treated as nickel anodes again, for concentration, this time with bags around the anode. The anode mud is then collected and sent to Acton, England, for the recovery of Pt, Pd, Rh, Ru; there is no gold nor silver.

The purification of the nickel sulfate electrolyte is by treatment in Pachuca [16a] tanks with nickel powder to precipitate copper, a Dorr thick-

[16a] A Pachuca tank is a tall tank 30 feet to 40 feet high, 14 feet in diameter, with a conical bottom, generally built of wood. A hollow column is set upright in the center of the tank. A stream of compressed air is fed in at the base of the column, driving the "pulp" or slurry upward, and causing it to descend in the wider part of the tank. The air circulation may be supplemented by a stirrer, or a pump, or both.

ener to remove remaining solids; oxidizers, followed by addition of nickel carbonate, to precipitate iron, and make good the resulting drop in p_H (rise in acidity); the electrolyte is kept at a p_H of 5.2. The liquor is filter-pressed, and is then ready to be fed back to the plating tanks. The capacity of the plant is 420,000 lbs. of 99.95 per cent nickel per day.

In the Mond recovery process, in operation in England, nickel in the metallic form is volatilized by means of carbon monoxide at 100° C. (212° F.), forming the gaseous $Ni(CO)_4$. Heated to 180° C. (356° F.), nickel carbonyl decomposes, leaving the metal behind; the monoxide may be used over again. The deposition is done in small towers, and on nickel shot from previous runs, which are screened to remove the larger sizes. The smaller sizes receive the new deposits, and acquire a structure very much like that of an onion. Before passing through the volatilizing tower, the ore goes through the reducing tower, similar to the system at Port Colborne, just described. The same ore passes reducing tower and volatilizing tower several times.

Over the year 1935, nickel was quoted at 35 cents a pound.

CHROMIUM

While fuel-fired furnaces have in the past produced an iron alloy with a maximum of 3 per cent chromium, the electric furnace produces alloys of any chromium content, even 99 per cent chromium. The uses for chrome steels and the importance of chrome plating have been discussed (Chapters 45 and 48). Nichrome is a nickel-chrome alloy, with high resistance to the electric current. Stellite contains chromium, cobalt (75 per cent) and tungsten; it is used for high-speed cutting tools, for gears, valves, lathe centers, etc. It is non-magnetic.

COLUMBIUM

In the treatment of stainless steels by columbium addition, in order to preserve their corrosion resistance even when heated, and to improve their suitability to welding, large quantities of the metal became necessary. Until recently, the stock of columbium consisted of museum samples. Since 1936 it is obtained in fairly large tonnage, from a deposit low in tantalum, from African columbite.[16a] A preliminary selective reduction is followed by chloridizing, in order to combine with tin, whose chloride then passes out by volatilization. The residue is reduced with aluminum, or silicon, in an electric furnace, with the production of a ferro-columbium containing 55 per cent Cb, suited to steel making. The production per annum is estimated at close to 500,000 pounds of columbium; all of it produced and consumed in the United States.

[16a] "Columbium, from a laboratory curiosity to a widely used commercial product," James H. Critchett, *Trans. Electrochem. Soc.*, **69**, 63 (1936). See Chapter 48.

ADDITIONAL PROPERTIES AND USES OF THE METALS; ALLOYS

The main use of copper is for electric motor and generator construction and for transmission lines, as stated in the introduction; it is also used for roofs, flashings, gutters, and conductor pipes; a copper roof coats itself with a layer of green carbonate and oxide which prevents further action. Lead when freshly scratched has a bright surface, which, however, tarnishes within a few minutes; lead is soft, and as such is used in the chemical industries [17] and for covering electrical cables placed underground and undersea. Lead is hardened by adding 1 to 10 per cent antimony. Lead and zinc for storage batteries and dry cells respectively have been mentioned. Both of these metals are made into pigments, and the interesting suggestion has been made, now that titanium pigments are available, that the lead be reserved for storage battery work, letting the titanium pigment replace white lead.[18] Lead wire is used for electrical fuses. A considerable use for zinc is in galvanizing; in 1935, 195,000 tons of zinc were used for this purpose in the United States. Tin plating is less important now than formerly. Lead (60 parts) and tin (40 parts) form the valuable and much-used solder. Nickel is electroplated on iron, or better, on iron previously plated with copper; the nickel coat has no luster until the article is buffed. A few statements concerning metals are condensed in Table 88.

TABLE 88.—*Properties of Metals. Price in Cents per Pound.*

	1929	1932	1935	May 1st, 1937	Color	Specific Gravity	Melting Point °F.	°C.	Electrical Conductivity
Copper	18.23	5.67	8.76	14.0	red	8.9	1891 or	1083	100
Lead	6.3	3.0	4.0	6.0	white	11.4	621 or	327	8
Zinc	6.49	2.88	4.33	6.75	white	7.2	786 or	419	27
Tin	45.19	39.12	50.39	55	white	7.3	450 or	232	12
Mercury ...	160.7	...	96	...	white	13.6	liquid		2

The alloys are very numerous, even of the type containing two metals only, for the proportions affect the properties materially; thus for brasses, the color is affected, as well as strength, ductility, hardness, and malleability. Brass consists of copper and zinc. Bronze is copper and tin, with perhaps a small amount of zinc. Bearing metal, such as Babbitt, contains tin, 89 per cent; antimony, 7 per cent; copper, 4 per cent (for Babbitt No. 1). There are other bearing metals in which copper is the main constituent, and still others which contain much lead; for example, Frary metal, 98 per cent Pb and 2 per cent Ba. Type metal must expand on cooling, so that the letters will be sharp; an example is the composition lead, 80 per cent; antimony, 20 per cent. Fusible alloys for fire extinguishers (automatic) contain tin, lead, bismuth, and either cadmium or antimony. Brasses are yellow to red; bronzes are brown; all the other alloys given above are white.

[17] Chapter 45.
[18] Chapter 31.

Other Patents

U. S. Patent 2,062,869, conducting chemical and metallurgical operations in a rotary furnace; 1,849,293 and 1,965,251, improvement to the indium plating bath; Canadian Patent 315,060, process of recovering nickel, Robert P. Stanley, assigned to the International Nickel Company, 18 claims.

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For many centuries, gold has been a synonym for wealth; to find gold, man will undergo untold hardships and risk his life, as demonstrated in the gold rush to California in 1849, through the desert; and again in the Klondike gold rush of 1896. In numerous mining and smelting processes, on the other hand, it is a humdrum operation, without excitement; the gold is just a by-product of copper. Gold is a unique commodity in that its price does not fluctuate with supply and demand, but is fixed by law. The former figure of $20.6718 per fine ounce was changed through decrees and legislation between August 9, 1933, and January 31, 1934, to $35.00. In terms of gold, the dollar is cheaper.

Chapter 50

Gold,* Silver, Platinum, Radium, Thorium, and Cerium

The unit in which prices for metals are quoted varies; pig iron is quoted by the ton; copper by the pound; but the precious metals are so valuable that they are quoted by the ounce. Gold has a fixed price, $35.00 a troy ounce (31.10 grams), the figure which superseded the previous one of $20.67, in 1934. Silver varies in price, but the United States government buys all offerings at 77.57 cents, in 1936 and 1937, while the 1935 figure was 71.11 cents, which may be compared with the 1930 open market figure of 38.47 cents a troy ounce. Platinum is in the neighborhood of $32 an ounce, while palladium is lower. Osmium, iridium, and rhodium are also precious metals. In a general way, the price reflects the scarcity of the metal; the scarcer the metal, the higher the price. The low price of iron reflects its abundance.

Radium belongs to the precious metals as far as price goes, but it is not prepared in the metallic form; it enters the market in the form of radium bromide, $RaBr_2$. It occurs in such small quantities and the extraction process is so long, that it is quoted in gram lots, in the neighborhood of $30,000 per gram. The total amount of radium in the world in the form of marketable salts is not over 250 grams (end of 1936).

Radium concludes the list of precious metals. The rare earth metals, such as thorium and cerium, rarely enter the market in the metallic form, but usually as manufactured articles, the oxides in the Welsbach gas mantles, the metals in pyrophoric (fire-producing) alloys. They may be considered as forming a special class which would include other rare earth metals, also tungsten, molybdenum, and perhaps vanadium and uranium.

The precious metal scrap is saved with great care and brings high prices; it is reworked into pure metals and useful shapes; as a result more finished metal is refined than the amount of ore mined would indicate.

* With the assistance of Mr. Reginald Williams, Gold expert, Buffalo, N. Y.

Gold and the platinum metals are found mainly in the free or metallic state (native metal); silver occurs partly native, partly as sulfide and other compounds. Native gold is rarely free from silver. In addition to deposits worked solely for their precious metals, there are many copper and lead ores which contain silver and gold, and these "values" are isolated in the process of refining.

GOLD

Gold deposits worked primarily for their gold content occur in many parts of the world, as indicated by Table 89: [1]

TABLE 89.—*World Deposits of Gold and Their Production, in Troy Ounces.*

	1932	1935
Transvaal	11,558,532	10,776,684
Rhodesia, West Africa, Congo, Madagascar	1,177,447	1,957,323
U. S. S. R.	1,990,085	5,831,106
United States	2,449,032	3,546,169
Canada	3,050,581	3,280,457
Australia, New Zealand	998,267	1,349,574
Japan	642,663	871,000
Mexico	584,487	682,257
China	225,707	343,000
British India	329,632	324,816
World total	24,150,761	31,279,386

Within the United States and territories, the distribution is shown in Table 90:

TABLE 90.—*United States Deposits of Gold and Their Production, in Troy Ounces.*

	1935	1936
California	890,430	1,049,600
South Dakota	567,230	590,679
Alaska	469,495	530,000
Colorado	349,281	364,713
Arizona	241,755	310,000
Nevada	188,031	284,700
Utah	184,838	224,500
Montana	151,088	179,000
Idaho	83,823	80,000
Oregon	54,160	59,900
Philippine Islands	451,814	599,000
United States and Philippines, Total	3,688,909	4,329,273

Gold occurs native in two kinds of deposits: hard ores which must be crushed to free the granules of gold, and alluvial gravel which may be dredged. The hard ores are generally "free-milling ores", that is, on crushing them under the hammers (stamps), the gold is freed enough to be extracted by amalgamation or by cyanide solution. The hard ores include the auriferous iron pyrite, in which the gold is in the free

state, and may be extracted by the cyanide solutions, without preliminary roasting, but not by mercury. In combined form the chief ore is the telluride. The second form in which gold-bearing material occurs is as alluvial deposits, chiefly gravels found in the beds of certain present rivers and of rivers of prehistoric times. Within the United States, about as much gold is obtained from lodes (that is, hard rocks) as from gravel. The gravel deposits are called placers, and may be mined for less money than the hard rocks, for the gravel does not require crushing.

Gold nuggets of various sizes have been found in several parts of the world, the largest containing 2284 ounces of gold (Victoria field, Australia), and give the impression that gold-bearing material is rich; but the opposite is true; nuggets are exceptional, and rich veins of gold are rare; the amount of gold in the ores is extremely low. Hard rocks with 1 part of gold to 70,000 parts of worthless gangue are common, while ores with 1 part in 300,000 [2] may still be worked at a profit. For placer deposits, the amount of gold may be still lower and still permit profitable operation.

Gold-bearing Quartz and Other Hard Rocks. Gold-bearing rocks are usually discovered by an outcrop, which soon leads into the ground so that shafts must be constructed and the ore lifted to the surface. It is crushed in gyratory [3] and jaw crushers,[3] or stamps, of which the latter are the older practice. A stamp battery consists of 5 hammers (stamps) with long stems; they are lifted by a cam, and drop by gravity onto the ore resting on a steel die at the bottom of a cast-iron crucible which accommodates 5 dies. Water enters from one side and leaves carrying the crushed rock on the other. The slurry may be worked for its gold in several ways; it is allowed to flow over slightly inclined amalgamated copper plates, which retain the gold, allowing the gangue, but also the auriferous pyrite, to pass. The discharge from the plates is then extracted with cyanide solution. Or, mercury may be added to the stamp crucible (direct amalgamation). The amalgam from the plates (scraped off) or from the stamps is pressed in soft leather or flannel bags to remove the liquid mercury, and the remaining amalgam is retorted. The product from gyratory and jaw crushers is treated similarly. Not infrequently, the crushed material is first concentrated on a shaking, inclined table over which water flows, carrying off the lighter gangue; the concentrates only are passed over the amalgamated plates.

Cyanide Process. The tailings from the amalgamated plates still contain some gold, which may be recovered by treating them with a cold sodium (or potassium) cyanide solution in the presence of air. It is becoming the custom to dispense with the amalgam method of recovery and treat the crushed ore directly with the cyanide solution. The ore is

[2] The South Dakota mines at Lead and Deadwood recover gold worth $3.50 per ton of rock; the Dome mine at Porcupine (Ontario) recovers gold worth $7.80 per ton (based on $20.67 an ounce).

[3] Chapter 44.

first reduced to fine powder in a ball mill, and the product is then agitated, cold, in a series of tanks, with a dilute cyanide solution:

$$4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH.$$
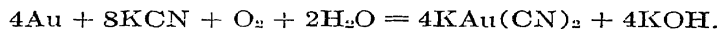
The cyanide method has among other advantages this one, mentioned before, that gold accompanied by pyrite may be extracted without roasting, after fine grinding.

The cyanide slurry is filter-pressed; the filtrate contains the gold. In order to isolate it, metallic zinc in the form of shavings is added; the gold powder with excess zinc is treated with sulfuric acid, which removes the zinc and leaves the gold. The latter is then melted with fluxes in a furnace and refined in any one of various ways. The precipitating reaction may be represented as follows:

$$2KAu(CN)_2 + 2Zn + 2H_2O = 2Zn(CN)_2 + 2Au + H_2 + 2KOH.$$
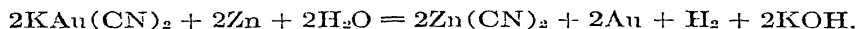
At some mines, the cyanide solution is passed into a pebble mill of the continuous type (Hardinge [4]) so that dissolving and pulverizing go on at the same time.

The cyanide solution leaving the zinc-gold is brought up to the standard strength, and is used over again.

Gold Telluride. Tellurides of gold are widely distributed, occurring for example at Cripple Creek, Colorado, in Calaveras County, California, and in western Australia. Calaverite is a bronze-yellow ore, $AuTe_2$, with a small amount of silver; 40 per cent Au, 56 per cent Te, 3.5 per cent and less Ag. Silver telluride with some gold (7 per cent or less) also occur. It must be roasted in a furnace in order to remove the tellurium as dioxide, before treating with cyanide.

Placer Mining. Placer mining furnishes about three-fourths of the world's gold; placers are the source of most of the gold in South Africa, Russia, the Klondike, and of part of the gold mined in California. The gold-bearing gravels at the surface of the earth are the result of the weathering and erosion of gold originally deposited in hard rock as lodes. It is reasonable therefore to look for a lode near-by when a gold-bearing gravel has been located; in many cases, the lode has been discovered. The large-scale method of operation is by dredging, washing the gravel on the boat, discharging the waste stones, and concentrating the gold from the sand on shaking tables. The dredge brings up the gravel by means of steel buckets on an endless chain; it is dumped into a trommel and rotated there while water is played on it; the sand passes through the perforations in the trommel and drops onto the shaking tables (also called classifiers) and concentrated there. The concentrates are carried to the extraction plant. Care is taken to dump the waste in one direction while the dredge moves forward in the other, so that no gravel will be reworked. One or two men operate the dredge.

Dredging is done not only on rivers which have a flow of water, but

[4] Chapter 44.

also in dry territory, provided water may be sent in by pipes from a river or lake not too far distant. A pit is dug, large enough to accommodate the dredge, and enough water pumped in to float it; operations then proceed as they would in a river.

Dredging is an extension of the hand operation called panning, still employed by prospectors and by individual operators without other equipment. The pan is a circular dish with a small pocket in the bottom; it is filled with gravel, and held under a gentle stream of water; on rotating it, the lighter parts are gradually floated off, and the gold particles are found in the pocket.
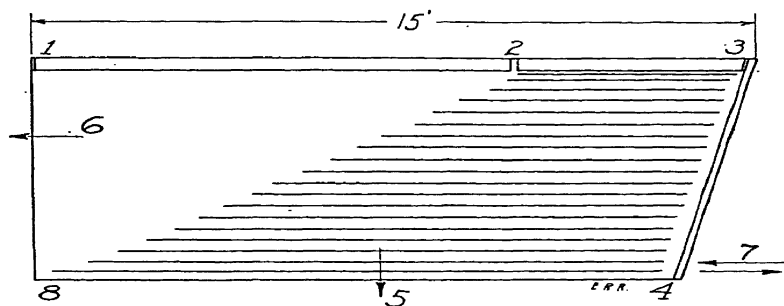
FIGURE 271.—Principle of a shaking table (Wilfley). Water enters from trough 1-2; slurry from 2-3; the table moves as shown by 7; 1-8 is several inches higher than 3-4, so that the concentrates move up-hill and are discharged at 6; the gangue goes off at 5. The table is covered with linoleum, on which the riffles are tacked as shown. Moving mechanism not drawn.

Hydraulic Mining. Another extension of panning is hydraulic mining, in which powerful streams of water discharged through nozzles as large as 11 inches in diameter are played in a solid column against the side of a hill whose gravel is gold-bearing. The gravel is floated along gullies to a sluiceway, an inclined plank floor with cross-pieces, against which the gold particles lodge. Once a week, or more often, the water is turned off and a "clean-up" performed; the cross-pieces are removed and the gold collected. Mercury may be added to the sluice box; it will lodge against the "riffles" also and retain the gold.

Gold is rarely free from silver; placer gold is generally purer than lode gold.

Gold may also be removed from crushed rock or gravel by chlorination.

Purification of Gold. The native metal or metal recovered from scrap may be purified from base metals such as lead by the furnace process called cupellation and described under silver.

In order to remove any silver in the gold, either a sulfuric or nitric acid treatment is performed, or an electrolytic method, that of Moebius, is employed. In the acid method, the silver is dissolved and leaves the

gold behind, but the protective action of the gold is so great that unless the silver present amounts to 80 per cent, the acid has no effect. Gold which contains less silver must first be melted with an extra amount before the separation from the silver, called the "parting," is effected.

The electrolytic method is the one usually employed in the United States. The anodes are doré silver, that is, gold-bearing silver; the cathode is a movable silver belt with a light coating of oil. The belt moves in a trough of redwood coated with an acid-resisting paint. The bath is silver nitrate kept slightly acid with nitric acid. The belt moves under the cathodes and is brushed off automatically at the turn, delivering silver powder. Each anode is hung in a fabric basket in which the gold slime deposits. The slimes are collected at intervals, washed with sulfuric acid, and melted for gold metal.

Properties and Uses of Gold. The pure metal may be hammered so thin that 250,000 sheets are required to make up 1 inch in thickness; the sheets are used for lettering book bindings. For coinage, gold is alloyed with copper, which hardens it; the pure metal is too soft for coinage purposes. The United States coinage is 900 fine [5] (900 parts gold and 100 parts copper). For jewelry, alloys with various proportions of gold are used, expressed in terms of carats; pure gold is 24 carat, 18 carat gold is 75 per cent gold. In dental work, gold is of great value, for it is unattacked by saliva or foods.

Gold is permanent in the air; it is unattacked by acids (except aqua regia and selenic acid); its characteristic yellow color is redder in copper alloys, greener in silver alloys. White gold is the palladium alloy.

SILVER

Silver is found alloyed with gold, and to a minor degree, as metallic silver enclosed in silver ores; the more general occurrence is in the form of compounds, and of these the sulfide of silver, argentite, is the principal ore. As stated under gold, much silver is recovered from copper and lead ore, during the refining process. It is interesting to note that in several localities in which gold, silver, and copper have been mined, the gold is above the silver, and the silver above the copper, so that a

TABLE 91.—*World Production of Silver, in Troy Ounces.*

	1932	1935
Mexico (Guanajuato, Sonora)	69,303,054	75,606,000
United States	23,980,773	44,825,000
South America (Peru, Bolivia, Chile)	11,190,661	23,500,000
Europe	13,144,462	16,475,000
Asia	13,719,511	15,820,000
Canada	18,356,393	15,763,000
Australia, New Zealand	9,492,726	12,310,000
Belgian Congo	1,864,700	3,900,000
Central America	4,300,000	3,000,000
World	166,927,841	213,753,000

[5] No longer binding by law; since April, 1933, the United States "have been off the gold standard," that is, the gold coin may be minted as low as 450 fine, at the discretion of the President.

mine started as a gold mine became a silver mine and later a copper mine as the depth of the shaft increased (Old Dominion Copper Company, Arizona). As with gold, much of the refined silver has its origin in silver scrap. The countries which produce the bulk of the new silver are indicated in Table 91.

It will be noted that the Transvaal, which leads in gold production, does not appear in the table; its silver production is only 1,047,000 ounces (1935). On the other hand Mexico, which is sixth in gold production, leads all other countries in silver produced. The production of Bolivia is slightly less than that of Germany, while that of Peru is five times greater than that of Spain. It will also be noted that the world's production of silver is much greater than that of gold. Within the United States and territories, the main producers are shown in Table 92.

TABLE 92.—*United States Production of Silver, in Troy Ounces.*

	1932	1935
Idaho	10,240,953	14,400,000
Montana	9,322,951	11,235,000
Utah	9,227,673	10,115,000
Arizona	6,601,280	8,125,000
Colorado	4,696,064	5,814,119
Nevada	4,393,426	4,970,000
California	1,191,112	2,026,700
Texas	1,000,960	1,383,000
New Mexico	1,061,902	1,141,000
United States, Philippines. Total	48,862,013	60,667,034

In Guanajuato, the ore is of the free-milling type, with the metal in the native state; this district is losing in importance, while a new Mexican center, Parral, in Chihuahua, is gaining.

For the sulfide ore, argentite, the process consists of a roasting on the hearth of a reverberatory furnace, followed by addition of charcoal and further heating to reduce the oxide to the free metal, which is run off in the molten state.

If the ore is lead-bearing, as it often is, more lead may be added until a free-flowing (easily melted) metal is obtained from the first ore treatment, and this lead alloy is put through the process of cupellation which removes the lead in the form of the oxide, PbO, litharge, leaving the silver metal on the hearth.

The cupel might be described as an open-hearth furnace with the hearth of special construction; it is made by ramming bone ash into an iron form; the bone ash is moistened with a potassium carbonate solution. In the center a shallow depression is scooped out. After drying, the cupel bottom is ready for use. Its function aside from furnishing a refractory base of non-contaminating material is to absorb a portion of the fused litharge, litharge solution of base metals, and liquid slags formed by the addition of fluxes. The greater part of the litharge is run off through a gutter and collected; if made from a rich alloy, it may retain some silver and must then be reduced again in the reverberatory furnace, and cupelled again; if made from a weak alloy, it enters the

market, and is used, for instance, for making the brilliant lead-potash glass for tableware. A lead alloy containing 500 ounces to the ton is considered a weak alloy; one containing 4000 ounces to the ton a rich one.

The process requires a blast of air directed onto the metals on the hearth, while at red heat. The end of the operation is reached when the last film of oxide is removed; the silver flashes out brightly, reflecting the arch of the furnace as a mirror would. The purity of the silver is 99.8 per cent, or 998 fine.

The cupel is used not only for silver but also for other precious metals; a silver-gold alloy is usually the result of cupellation. Bone-ash crucibles may be used as well as a hearth of bone ash.

Silver is prized for its beautiful color; its surface takes a high polish. Its uses depend in part upon its superior color and its stability in the air (jewelry, tableware). Silver coins usually contain 5 to 10 per cent copper.

An important use of silver is in photography,[6] in the form of silver bromide and chloride, sensitive to light; another commercial use of silver salts (the nitrate) is in making mirrors.[7]

Indium. It was discovered that the addition of indium to silver renders such silver, whether solid silver or plated ware, tarnish-proof.[8] The indium may be incorporated in the silver by hanging two cathodes, one an indium rod, one a silver rod, in the plating bath, with the two double salts of potassium cyanide and indium and silver, dissolved in the plating bath; the object to be plated forms the cathode. With a density of .07 ampere per square inch, a deposit of 4 to 5 per cent indium is formed. By raising the current density to .1, a deposit with 11 per cent indium is formed. By varying the current density, the proportion of indium may be varied at will. A second method is to deposit alternate layers of silver and indium, and then to heat in an oven in order to allow the metals to diffuse. A bluish color which the indium imparts to silver is counteracted by a further improvement, namely, by depositing a silver-gold alloy [8a] instead of silver, and alternating with indium. For example, $12\frac{1}{2}$ per cent gold, $87\frac{1}{2}$ per cent silver, alternating with indium, heating first to 110° C. (230° F.) for 8 hours, then to 165° C. (329° F.) for 18 hours. The yellow of the gold neutralizes the blue of the indium. The electrodeposition of indium is facilitated by the addition to the plating bath of an organic compound of an acid nature which has the effect of retaining the indium salt in solution, while without it, it tends to separate from the bath [8b]; such a compound is glycine. The current density recommended in one example for the glycine-containing bath is .035 ampere per square inch.[8c]

Indium plated on copper also produces a tarnish-proof surface.[8d]

[6] Chapter 37.
[7] Chapter 11.
[8] Canadian Patent 338,197 and U. S. Patents 1,959,668; 1,847,941.
[8a] U. S. Patent 1,934,730.
[8b] U. S. Patent 1,935,630.
[8c] For the source and extraction of indium, see chapter 49.
[8d] U. S. Patent 1,960,740.

PLATINUM

Platinum is a white metal, more resistant to chemical agents than silver but not more beautiful in color. It is much heavier than silver (21.5 against 10.5). The production of platinum is usually less than that of gold. Formerly platinum was considered of no value [9]; with the development of chemical analysis, it was found that platinum vessels resisted heat and the action of most chemical reagents except aqua regia which dissolves it slowly, and some others.[10] For many years, sulfuric acid made in the lead chambers was concentrated in platinum pans; at the present time, it functions in a new way in the manufacture of the same acid, namely, as a catalyst.[11] Platinum is used extensively in jewelry. Among the many other services which this metal renders, its use in pyrometers must not be overlooked.

Platinum occurs nearly altogether as a native metal, alloyed with palladium, iridium, in alluvial deposits chiefly.[12] The principal regions of production are shown in Table 93:

TABLE 93.—*World Production of Platinum, in Troy Ounces.*

	1933	1934	1935
U. S. S. R.	150,451	70,689	130,000
Canada	24,786	116,230	105,374
South Africa	6,880	27,480	24,900
Ethiopia	6,650	5,612	5,175
United States	1,298	2,976	6,593
World total	240,000	280,000	313,000

In the United States the small amount of primary platinum in former years was a by-product of California placer gold; the increased production is due to workings on Squirrel Creek, Goodnews Bay, Alaska, started in 1935, and expected to yield 10,000 ounces annually.

The Russian production comes from the Ural Mountains, where there are several districts; the most important ones at the present time are those of the two rivers, the Iss and the Wija, which combine to form the Tura. The gravels of the river beds carry the platinum values over a distance of about 90 miles. The recovery is by hand panning, or by placer mining.

The platinum produced in Columbia is mainly a by-product of gold production, by panning or placer mining. Platinum is also recovered in the process of refining copper (Anaconda) and nickel ores.

The Russian crude platinum contains iron; nearly all platinum from placer mining carries iridium, and some also osmium, palladium, and

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[9] In the 18th century, a boat-load of platinum brought to Spain from the new world was ordered sunk as valueless. The earliest record of the incident discovered to date is one in Diderot and d'Alembert's "Encyclopédie ou Dictionnaire raisonné de Sciences," published 1778; tome XXV, p. 187: "On assure que le roi d'Espagne a fait fermer ces mines (de Santaje et de Popayan) et a fait jeter à la mer une très grande quantité de platines pour prévenir les abus que ses sujets en faisoient."

[10] Phosphorus, arsenic, and bismuth compounds, alkali cyanides and sulfides, carbon from a smoky flame, attack platinum.

[11] Chapter 1.

[12] Alluvial deposits are secondary deposits; the original platinum-bearing rock has weathered and has been moved by water.

other impurities. Iron is removed by hydrochloric acid. Platinum, palladium, and iridium may be separated by solution in aqua regia and heating the chlorides formed to 125° C.; from the solution of the resulting chlorides, ammonium chloride precipitates the platinum. It is reduced to platinum black, which is fused in the electric furnace or in the hydrogen-oxygen flame to the metal. The platinum prepared in this way retains about 2 per cent iridium, which is desirable, for the iridium hardens it.

The precious metals must be melted in the course of the manufacture of sheets, foils, wires, and shapes of various kinds, in order to form alloys of suitable compositions, or for remelting the cuttings and end-pieces, or for a purification. This may be done in an induction furnace, rapidly, and without danger of contamination by even gaseous fuel. The induction furnace [13] consists of a fire-clay crucible, for example, 3 inches in diameter, which is set in a coil of one-fourth inch iron pipe through which cold water circulates, plastered with asbestos mud in which the primary winding is placed. The metal scrap in the crucible is the secondary. A current of 250 volts (15 kilowatts) is transformed to 8000 volts in a transformer with reactance, and delivered to a condenser with a discharge gap; a frequency o˙ 30,000 to 50,000 cycles (per second) is obtained. On connecting the primary, the metal begins to glow in a few seconds, and melts in 2 minutes or so, while the crucible remains cold to the touch. The liquid metal is violently agitated by the induced current.[14] A temperature of about 5500° F. (3038° C.) may be attained. By placing the crucible and furnace under a glass bell-jar and connecting it to a strong suction pump, occluded gas may be completely removed, an important precaution in n ˙rials for dental alloys.

The usual method of melting platinum is to place the metal pieces in a cavity in a two-piece block of lime, and to introduce the oxy-hydrogen flame (or the oxygen-gas flame) through an opening in the upper half of the lime block; the necessary high temperature, 3191° F. (1755° C.), the melting point of pure platinum, is thus reached.

In 1935, the consumption of platinum in the United States was 125,064 troy ounces, imported as metal, as crude platinum, in the form of ores and concentrates, from gold and copper refining, from domestic scrap and mine production, all included; of this total, 11 per cent was used in the chemical industries, 10 in the electrical, 25 in the dental supply manufacture, 52 in jewelry, and the rest miscellaneous. For that year, (1935), platinum averaged $32.60, palladium $23.25, Iridium $50.90, Osmium $51.00, Rhodium $44.00, Ruthenium $39.00 an ounce.

Radium Bromide

Radium was originally concentrated from pitchblende, a uranium oxide ore found in Joachimstahl, in the northwestern part of Czecho-

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[13] The practice at the Williams Gold Refinery Works, of Buffalo, N. Y.

[14] The order in which the metals melt in the induction furnace is the order of their resistivity; the higher it is, the faster the metal melts.

slovakia. In the United States, it was concentrated in Pittsburgh, from carnotite, a sandstone impregnated with uranium vanadate. Radium is always found associated with uranium ores; it is a disintegration product of uranium. At the present time, the American mines and plants are not operated, because the low-grade American ores cannot compete with the high-grade ore from Katanga, in the Belgian Congo. Since 1923, ore from Katanga has been shipped to Belgium and there treated.

It was only for a short time, however, that the Katanga ore headed the market; it has now been displaced in point of richness by the pitchblende deposits on LaBine Point, named after the discoverer Gilbert

FIGURE 272.—The site of the radium ore deposit and the mining camp, Eldorado Mines, in 1937, seven years after the discovery. Great Bear Lake, Point LaBine, Mackenzie, Canada. (Eldorado Mines, Canada.)
   In these sub-Arctic hills, 26 miles from the Arctic Circle, on the shores of Great Bear, the largest freshwater lake lying wholly within the British Empire, the richest known deposit of radium lay concealed for many centuries. In 1930, Gilbert LaBine discovered the pitchblende veins which contain radium and uranium. By 1937, this flourishing mining camp, Eldorado Mines, had grown up on the site.

LaBine, on the eastern edge of Great Bear Lake, Northwest Territories, Mackenzie District, Canada, and just south of the Arctic Circle. The discovery was in 1930. The main deposit is a vein 1400 feet long which on analysis of official samples was shown to run 62 per cent U_3O_8. The radium content indicates the richness of the ore: there were required 128 tons of the Colorado carnotite to produce 1 gram of radium; of the Katanga ore, 10 tons for the strongest, with an average of 30 to 40 tons. The Great Bear Lake ore is expected to yield 1 gram of radium from only six and a half tons. Theoretically, a 100 per cent U_3O_8 ore con-

tains 1 gram of radium in 4 tons. The ore is concentrated at the mine, then flown to Edmonton (1000 miles) and thence shipped to Port Hope, Ontario (1500 miles) by rail.

The method of recovering radium and uranium is to concentrate the ore, roast the crushed concentrate with salt, reduce it, leach it with hot sulfuric acid, and add barium chloride. The radium precipitates with
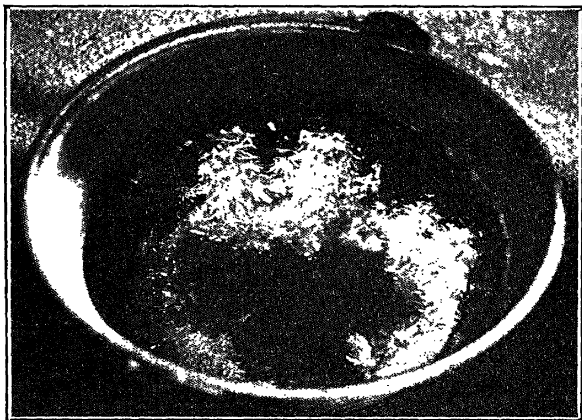
FIGURE 273. — Radium-barium bromide crystals forming during cooling in the Monel pail. The last stages of radium refining at the Eldorado Mines' refinery at Port Hope, Ontario, consists of 23 processes of fractional crystallization, based on the method used by Madame Curie. During these operations, the infinitesimal amounts of the rare substance are slowly liberated from the barium which has been added to enable the workers to keep track of the radium. (Eldorado Mines, Canada.)

the barium, lead and silver; the uranium is in solution. The precipitate is boiled with soda ash, to form the carbonates; these are filtered, and on treatment with hydrochloric acid, radium and barium dissolve, and are made into the double bromide. Fractional crystallization gives a radium bromide with 90 to 95 per cent $RaBr_2$. Radium bromide is a white solid, soluble in water. The uranium solution gives a sodium uranate, or oxides or other salts. Beginning with June 1937, the production at Port Hope will be at the rate of 6 grams of radium per month. The total store of radium available for therapy in the world is about 250 grams.

Much of the Canadian ore contains leaf silver; some contains also rhodochrosite, a manganese carbonate; other veins are high in silica and free from carbonates.

Just what the price will be is not certain, but a reduction will be welcomed, inasmuch as it will make radium therapy available to all. The original price of $100,000 a gram was sharply reduced upon the discovery of the Katanga deposits; the Great Bear Lake deposit should lead to a figure below $29,000. There is as a by-product uranium oxide, which is sold for $1.30 per pound of U_3O_8, a price which should allow many new uses now unknown.

For use in therapy, the radium bromide is generally converted to the sulfate, and put up in small lots of capillary glass of gold tubes. Another method is to preserve the water solution in a glass system, and pump off every day the gaseous emanation into small glass bulbs, also suitable

for the treatment of patients. The standard of strength for either kind is the milli-curie,[15] measured on the gamma-electroscope.

Radium salts are also used in luminous paints mixed with intensifying admixtures such as zinc sulfide or calcium sulfide.

<center>THORIUM AND CERIUM</center>

The Welsbach mantle [16] for gas light consists of thoria, ThO_2, and 1 or 2 per cent ceria, CeO_2, obtained from monazite sand found in Brazil (the best) and North Carolina and West Virginia. In order to extract thoria and ceria, the sand, washed free from earth, is freed from iron by passing it over electromagnets with low current, from garnet by the same electromagnets with high current. The remaining material is treated with sulfuric acid and from this solution the oxalates are precipitated; thorium oxalate is separated by solution in ammonium oxalate, in which cerium oxalate is not soluble. Both are refined further and transformed into the nitrates; these are dissolved and mixed to give the relative amounts corresponding to the figures above. In order to make

FIGURE 274.—After 93 men in the mines at Great Bear Lake have worked two weeks to produce many tons of ore; after 48 men in the refinery have worked another two weeks, the precious radium material has been reduced to the group of crystals in this single glass flask in the hands of a worker. (Courtesy of the Eldorado Mines, Canada, through Mr. L. E. Westman, Toronto, Canada.)

the mantle, a weave of cotton or rayon is soaked with the solution of the nitrate mixture, dried, and ignited. The resulting shape consists of the oxides; it is dipped in collodion to stiffen it for transport. Soft mantles are also made. The Welsbach mantles will probably always remain of great importance for lighting in isolated places, such as lighthouses on the seacoast.

[15] The milli-curie is the radio activity of 1 milligram of radium in equilibrium with its disin-

[16] The Welsbach plant at Camden N. J.; *Chem. Met. Eng.,* **21,** 497 (1919).

After the thorium salts are removed, and some of the cerium, there is obtained as a by-product a mixture of the salts of cerium, lanthanum, didymium, yttrium, and samarium. These salts are changed to the chlorides, and placed, gradually, in an iron crucible forming the cathode, in which a carbon anode dips. The crucible is heated just at the bottom to fuse the chlorides. There is obtained a button on the bottom of the crucible consisting of cerium with the other metals named as admixtures. The button is alloyed with 30 per cent iron and made into small pieces one-eighth inch in diameter and 1 inch long, mounted for cigar-lighters. When scratched with a piece of iron, sparks are produced; this is the pyrophoric alloy.[17]

FIGURE 275.—Until a few years ago, all the vanadium ore from the Minas Ragva was transported on the backs of llamas to the nearest shipping point. (Courtesy of Dr. B. D. Saklatwalla, of the Vanadium Corporation of America.)

Metallic thorium has been prepared, although not on an industrial scale; a very complete reference is given below.[18]

Tungsten in the United States is obtained chiefly from wolframite, a tungstate of iron and manganese found in Colorado.[18a] Ferrotungstate is manufactured, but also the metal, by forming the tungstic acid, calcining, and reducing with carbon. Tungsten filaments may be made from the metal mixed with sugar, and drawn into a wire which is then heated in

[17] U. S. Patent 1,273,223; compare also *Ind. Chem. Eng.*, **10**, 849 (1918).

[18] "Metallic thorium," J. W. Marden and H. C. Rentschler, *Ind. Eng. Chem.*, **19**, 97 (1927).

[18a] The main producers for the world in the order of their importance are: Kiangsi province, China, Burma, United States, Malay states, Portugal.

an atmosphere of hydrogen; they may also be made by the substitution process, in which a carbon filament is heated in an atmosphere of tungsten oxychloride mixed with hydrogen.[19]   Tungsten is required for making the carbide, which is used as a cutting tool, for sand blast nozzles, and wire drawing dies. Tungsten steel for cutting tools has been mentioned in Chapter 48.

Steel, brass, nickel, or silver articles may be tungsten plated in an alkaline solution containing dissolved tungstic oxide (WO_3) with 1 per cent of its weight of nickel in solution.[20]   Without the nickel, the deposition of tungsten stops after a very thin layer has formed, through self-polarization. The article to be plated is made the cathode, while the anode may be platinum.

Vanadium, in the form of ferro-vanadium, finds its chief industrial use in the manufacture of special steels for automotive and other purposes to which it confers unusual strength and resistance to fatigue. The main ores are the patronite, a sulfide of vanadium found in Peru not far from the Cerro de Pasco copper deposits, and carnotite in Colorado. It has been shown that chemically vanadium resembles tantalum, and not antimony and bismuth.[21]

OTHER PATENT

U. S. Patent 2,029,387, agent to improve the metal deposit from a plating bath.

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[19] "Tungsten refining in Europe," C. Matignon, *Chem. Met. Eng.*, 23, 697 (1920).
[20] U. S. Patents 1,885,702; 1,885,701; 1,883,235.
[21] *Ind. Eng. Chem.*, 19, 787 (1927), J. W. Marden and M. N. Rich.

Appendix

*Table of the More Important Chemical Elements with Their Symbols and
Atomic Weights*

(From the International Table of Atomic Weights for 1925)

Aluminum	Al	26.97	Manganese	Mn	54.93
Antimony	Sb	121.77	Mercury	Hg	200.61
Argon	A	39.91	Molybdenum	Mo	96.0
Arsenic	As	74.96	Neon	Ne	20.2
Barium	Ba	137.37	Nickel	Ni	58.69
Bismuth	Bi	209.0	Nitrogen	N	14.008
Boron	B	10.82	Osmium	Os	190.8
Bromine	Br	79.92	Oxygen	O	16.000
Cadmium	Cd	112.41	Palladium	Pd	106.7
Calcium	Ca	40.07	Phosphorus	P	31.027
Carbon	C	12.000	Platinum	Pt	195.23
Cerium	Ce	140.25	Potassium	K	39.096
Cesium	Cs	132.81	Radium	Ra	225.95
Chlorine	Cl	35.46	Radon	Rn	222.
Cromium	Cr	52.01	Rhodium	Rh	102.91
Cobalt	Co	58.94	Selenium	Se	79.2
Copper	Cu	63.57	Silicon	Si	28.06
Fluorine	F	19.0	Silver	Ag	107.880
Gold	Au	197.2	Sodium	Na	22.997
Helium	He	4.00	Strontium	Sr	87.63
Hydrogen	H	1.008	Sulfur	S	32.064
Iodine	I	126.932	Thorium	Th	232.15
Iridium	Ir	193.1	Tin	Sn	118.70
Iron	Fe	55.84	Titanium	Ti	48.1
Krypton	Kr	82.9	Tungsten	W	184.0
Lanthanum	La	138.90	Uranium	U	238.17
Lead	Pb	207.20	Vanadium	V	50.96
Lithium	Li	6.940	Zinc	Zn	65.38
Magnesium	Mg	24.32	Zirconium	Zr	91.

Table for Conversions

1 meter = 39.37 inches
1 foot = 304.80 millimeters
1 inch = 25.40 millimeters
1 pound =453.6 grams
1 cubic foot = 28.315 liters; 1 cubic foot of water at 62° F. weighs 62.321 pounds.
1 cubic foot contains 7.48 gallons (U. S.) ; 1 cubic meter = 35.3166 cu. ft.
1 gallon (U. S.) of water weighs 8.33 pounds.
1 gallon (English) of water weighs 10.0 pounds.
1 kilometer = 0.6214 mile.
1 gross ton =1 long ton = 2200 pounds.
1 short ton = 1 net ton = 2000 pounds.
1 metric ton = 1000 kilograms = 2205 pounds.

1 square meter = 10.7631 square feet.
1 ounce avoirdupois = 28.35 grams.
1 ounce troy = 31.10 grams.

1 gram mole of a gas at S.T.P. = 22.4 liters   .791.
$1 \mu = 10^{-6}$ meter $= 10^{-4}$ centimeter $= 10^{-3}$ millimeter
$1 m\mu = 10^{-6}$ millimeter $= 10$ A.U.

To change centigrade degrees to Fahrenheit degrees, multiply by 9/5 and add 32.
The British Thermal Unit (Btu.) is the quantity of heat necessary to raise 1 pound of water 1° F. from 60 to 61°; it also equals 777.52 foot-pounds.
The large Calorie, also called the kilogram calorie (Cal), is the amount of heat necessary to raise 1 kilogram of water 1° C. from 17 to 18°.
1 Cal = 3.968 Btu.   970 Btu. are required to vaporize 1 pound of water at 212° F. to steam at 212° F.
The specific heat of water is 1.

---

1 horsepower = 0.7457 kilowatt.
1 kilowatt = 1.341 horsepower.
Horsepower and kilowatts require a time factor to mean a quantity of power.
1 horsepower-hour = 0.7457 kilowatt-hour.
1 horsepower-second = 550 foot-pounds.

---

1 pound pressure is equivalent to a column of water 2.304 feet high.
Normal atmospheric pressure at sea level is 14.70 pounds per square inch and supports a column of mercury 29.92 inches high at 15° C., or a column of water 33.93 feet high at 15° C., which is also the maximum lift on the suction side of a pump. 29.92 inches = 760 milimeters.

---

1 volt times 1 ampere equals 1 watt.
1000 watts equal 1 kilowatt.
1 ampere-second deposits 0.001118 grams of silver.

Note: The pound in this table is the avoirdupois pound in every case. Unless otherwise specified, this is the pound meant in ordinary affairs.

Tables on heat values of fuels and on specific gravities of metals and alloys, will be found in the text.

For calculation of costs, consult:
"The technical organization, its development and administration," John Morris Weiss and Charles Raymond Downs, McGraw-Hill Co., New York, **1914.**

The number called p_H is a negative exponent of 10; 10 with that exponent, times 1, gives the amount of hydrogen ions, in grams, in 1 liter of the solution.

A cord of wood is a pile 8 feet long, 4 feet wide, and 4 feet high.

Specific Gravity Equivalents for Degrees Baumé for Liquids Heavier than Water

* Temperature 60°/60° F.
One gallon distilled water at 60° F. in air = 8.32823 lbs.
Table adopted by the U. S. Bureau of Standards from the formula:

$$° \text{Baumé} = 145 - \frac{145}{\text{Sp. Gr.} \frac{60°}{60°} \text{F.}}$$

Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon	Degrees Baumé	Specific Gravity 60°/60° F	Pounds per Gallon
0.	1.0000	8.328	36.	1.3303	11.079
1.	1.0069	8.385	37.	1.3426	11.181
2.	1.0140	8.445	38.	1.3551	11.285
3.	1.0211	8.504	39.	1.3679	11.392
4.	1.0284	8.565	40.	1.3810	11.501
5.	1.0357	8.625	41.	1.3942	11.611
6.	1.0432	8.688	42.	1.4078	11.724
7.	1.0507	8.750	43.	1.4216	11.839
8.	1.0584	8.814	44.	1.4356	11.956
9.	1.0662	8.879	45.	1.4500	12.076
10.	1.0741	8.945	46.	1.4646	12.197
11.	1.0821	9.012	47.	1.4796	12.322
12.	1.0902	9.079	48.	1.4948	12.449
13.	1.0985	9.148	49.	1.5104	12.579
14.	1.1069	9.218	50.	1.5263	12.711
15.	1.1154	9.289	51.	1.5426	12.849
16.	1.1240	9.361	52.	1.5591	12.984
17.	1.1328	9.434	53.	1.5761	13.126
18.	1.1417	9.508	54.	1.5934	13.270
19.	1.1508	9.584	55.	1.6111	13.417
20.	1.1600	9.660	56.	1.6292	13.568
21.	1.1694	9.739	57.	1.6477	13.722
22.	1.1789	9.818	58.	1.6667	13.880
23.	1.1885	9.898	59.	1.6860	14.041
24.	1.1983	9.979	60.	1.7059	14.207
25.	1.2083	10.063	61.	1.7262	14.376
26.	1.2185	10.148	62.	1.7470	14.549
27.	1.2288	10.233	63.	1.7683	14.727
28.	1.2393	10.321	64.	1.7901	14.908
29.	1.2500	10.410	65.	1.8125	15.095
30.	1.2609	10.501	66.	1.8354	15.285
31.	1.2719	10.592	67.	1.8590	15.482
32.	1.2832	10.686	68.	1.8831	15.683
33.	1.2946	10.781	69.	1.9079	15.889
34.	1.3063	10.879	70.	1.9333	16.101
35.	1.3182	10.978			

* All densities taken at 60° F. and referred to distilled water at 60° F. as 1.0000.

APPENDIX

Degrees Baumé with Corresponding Specific Gravity for Liquids Lighter than Water *

$$^\circ \text{Baumé} = \frac{140}{\text{sp. gr. } 60^\circ/60^\circ \text{ F.}} - 130, \text{ at } 60^\circ \text{ F.}$$

Degrees Baumé	Specific Gravity 60°/60° F.	Pounds per Gallon	Degrees Baumé	Specific Gravity 60°/60° F.	Pounds per Gallon
10.0	1.0000	8.328	55.0	0.7568	6.300
11.0	.9929	8.269	56.0	.7527	6.266
12.0	.9859	8.211	57.0	.7487	6.233
13.0	.9790	8.153	58.0	.7447	6.199
14.0	.9722	8.096	59.0	.7407	6.166
15.0	.9655	8.041	60.0	.7368	6.134
16.0	.9589	7.986	61.0	.7330	6.102
17.0	.9524	7.931	62.0	.7292	6.070
18.0	.9459	7.877	63.0	.7254	6.038
19.0	.9396	7.825	64.0	.7216	6.007
20.0	.9333	7.772	65.0	.7179	5.976
21.0	.9272	7.721	66.0	.7143	5.946
22.0	.9211	7.670	67.0	.7107	5.916
23.0	.9150	7.620	68.0	.7071	5.886
24.0	.9091	7.570	69.0	.7035	5.856
25.0	.9032	7.522	70.0	.7000	5.827
26.0	.8974	7.473	71.0	.6965	5.798
27.0	.8917	7.425	72.0	.6931	5.769
28.0	.8861	7.378	73.0	.6897	5.741
29.0	.8805	7.332	74.0	.6863	5.712
30.0	.8750	7.286	75.0	.6829	5.685
31.0	.8696	7.241	76.0	.6796	5.657
32.0	.8642	7.196	77.0	.6763	5.629
33.0	.8589	7.152	78.0	.6731	5.602
34.0	.8537	7.108	79.0	.6699	5.576
35.0	.8485	7.065	80.0	.6667	5.549
36.0	.8434	7.022	81.0	.6635	5.522
37.0	.8383	6.980	82.0	.6604	5.497
38.0	.8333	6.939	83.0	.6573	5.471
39.0	.8284	6.898	84.0	.6542	5.445
40.0	.8235	6.857	85.0	.6512	5.420
41.0	.8187	6.817	86.0	.6482	5.395
42.0	.8140	6.777	87.0	.6452	5.370
43.0	.8092	6.738	88.0	.6422	5.345
44.0	.8046	6.699	89.0	.6393	5.320
45.0	.8000	6.661	90.0	.6364	5.296
46.0	.7955	6.623	91.0	.6335	5.272
47.0	.7910	6.586	92.0	.6306	5.248
48.0	.7865	6.548	93.0	.6278	5.225
49.0	.7821	6.511	94.0	.6250	5.201
50.0	.7778	6.475	95.0	.6222	5.178
51.0	.7735	6.440	96.0	.6195	5.155
52.0	.7692	6.404	97.0	.6167	5.132
53.0	.7650	6.369	98.0	.6140	5.110
54.0	.7609	6.334	99.0	.6114	5.088
55.00	.7568	6.300	100.0	.6087	5.066

* Bureau of Standards, Circular No. 57.

Degrees A.P.I. (American Petroleum Institute) and Corresponding Specific Gravity for Petroleum Oils, Mainly for Liquids Lighter Than Water, at 60° F. Referred to Water at 60° F.*

$$\text{Degree A.P.I.} = \frac{141.5}{\text{sp. gr. } 60°/60° \text{ F.}} - 131.5$$

Degrees A.P.I.	Specific Gravity 60°/60° F	Pounds per Gallon	Degrees A.P.I.	Specific Gravity 60°/60° F	Pounds per Gallon
10.00	1.0000	8.328			
11.00	.9930	8.270	56.00	.7547	6.283
12.00	.9861	8.212	57.00	.7507	6.249
13.00	.9792	8.155	58.00	.7467	6.216
14.00	.9725	8.099	59.00	.7428	6.184
15.00	.9659	8.044	60.00	.7389	6.151
16.00	.9593	7.989	61.00	.7351	6.119
17.00	.9529	7.935	62.00	.7313	6.087
18.00	.9465	7.882	63.00	.7275	6.056
19.00	.9402	7.830	64.00	.7238	6.025
20.00	.9340	7.778	65.00	.7201	5.994
21.00	.9279	7.727	66.00	.7165	5.964
22.00	.9218	7.676	67.00	.7128	5.934
23.00	.9259	7.627	68.00	.7093	5.904
24.00	.9100	7.578	69.00	.7057	5.874
25.00	.9042	7.529	70.00	.7022	5.845
26.00	.8984	7.481	71.00	.6988	5.817
27.00	.8927	7.434	72.00	.6953	5.788
28.00	.8871	7.387	73.00	.6919	5.759
29.00	.8816	7.341	74.00	.6886	5.731
30.00	.8762	7.296	75.00	.6852	5.703
31.00	.8708	7.251	76.00	.6819	5.676
32.00	.8654	7.206	77.00	.6787	5.649
33.00	.8602	7.163	78.00	.6754	5.622
34.00	.8550	7.119	79.00	.6722	5.595
35.00	.8498	7.076	80.00	.6690	5.568
36.00	.8448	7.034	81.00	.6659	5.542
37.00	.8398	6.993	82.00	.6628	5.516
38.00	.8348	6.951	83.00	.6597	5.491
39.00	.8299	6.910	84.00	.6566	5.465
40.00	.8251	6.870	85.00	.6536	5.440
41.00	.8203	6.830	86.00	.6506	5.415
42.00	.8155	6.790	87.00	.6476	5.390
43.00	.8109	6.752	88.00	.6446	5.365
44.00	.8063	6.713	89.00	.6417	5.341
45.00	.8017	6.675	90.00	.6388	5.316
46.00	.7972	6.637	91.00	.6360	5.293
47.00	.7927	6.600	92.00	.6331	5.269
48.00	.7883	6.563	93.00	.6303	5.246
49.00	.7839	6.526	94.00	.6275	5.222
50.00	.7796	6.490	95.00	.6247	5.199
51.00	.7753	6.455	96.00	.6220	5.176
52.00	.7711	6.420	97.00	.6193	5.154
53.00	.7669	6.385	98.00	.6166	5.131
54.00	.7628	6.350	99.00	.6139	5.109
55.00	.7587	6.316	100.00	.6112	5.086

* Bureau of Standards, Circular C 410.

DIESEL FUEL STANDARDS

The following specifications for Diesel Oils are given because these fuels are comparatively new, and it is difficult to find specifications for them in the usual collections.

Criteria of Diesel Fuels, Their Relative Importance, L. J. Le Mesurier, Anglo-Iranian Oil Co. Petroleum Times 37, 85 (1937), Jan. 16.

Following are three specifications that have been considered by the British Standards Institution:

"Grade A—For automotive or other similar types of engines with small cylinders. Speed above 800 r.p.m. and high standard of performance essential.

"Grade B—For medium speed engines and powers not less than 25 b.h.p. per cylinder. For example, industrial units and main and auxiliary marine engines.

"Grade C—For large slow-running engines where adequate provision is made for heating and cleaning the fuel.

Grade		A	B	C
Flash point	Minimum	150° F.	150° F.	150° F.
Aniline point*	Minimum	60° C.	45° C.	...
Hard asphalt	Maximum	0.01%	2.0%	4.0%
Conradson carbon	Maximum	0.2%	4.0%	8.0%
Ash	Maximum	0.01%	0.05%	0.10%
Viscosity redwood No. 1 at 100° F.	Maximum	45"	100"	750"
Pour point	Maximum	20° F.	...	
Sulfur content	Maximum	1.0%	2.0%	1.0%
Water content	Maximum	Not to exceed 0.1%	0.5%	1.0%
Distillation. Vol. to 350° C.	Minimum	85%	...	...
Calorific value, gross	Minimum	19,250	18,750	18,250

* Approximate measure of ignition quality pending the development of a standard engine test."

Navy Department Specification for Diesel Fuel. Specification No. 7-0-2c, August 1, 1936.

"B.   Grade B-1.   Fuel oil for Diesel engine shall be furnished in one grade only.

"C.   Material and Workmanship, etc. C-1. Diesel fuel oil shall be a petroleum distillate.   It shall be free from grit, acid, and fibrous or other foreign matter likely to clog or injure pumps, nozzles, or valves.

"E.   Detail Requirements.   E-1.   Fuel oil for Diesel engines shall conform to the following chemical and physical characteristics:

| Test | Test No. | | Limit |
	F.S.B.	A.S.T.M.	
Flash point, closed cup, °F., minimum........	110.22	D93–22	150
Pour point, °F., maximum	20.14	D97–33	0
Viscosity, SSU, at 100° F.	30.43	D88–33	35–45
Water and sediment, per cent, maximum......	300.32	D96–30	0.05
Total sulfur, per cent, maximum	520.22	D129–33	1.0
Carbon residue, per cent, maximum..........	500.13	189–30	0.2
Ash, per cent, maximum	542.1	.....	0.01
Corrosion at 212° F., copper strip	530.31	.....	(1)
90 per cent distillation temperature, °F., maximum	100.14	D86–30	675
Diesel index number, minimum	.....	.....	(2)45
A.P.I. gravity	40.1	D287–33	
Aniline point	310.11		

(1) Negative.   (2) See F-4.

"F.   Methods of Sampling, Inspection, and Tests.

F-1. Sampling.—Samples shall be taken according to the procedure described in Section F of Federal Specification VV-L-791, referred to in Section A.

F-2. Inspection and tests.—Unless otherwise specified, all tests shall be made according to the methods for testing contained in section F of Federal Specification VV-L-791.

F-3. Diesel index number.—The Diesel index number shall be determined by the following equation:

$$\text{Diesel index number} = \frac{\text{aniline point (°F.)} \times \text{A.P.I. gravity}}{100}$$

The aniline point shall be determined in °F. by the method described as part of method 310.11, Federal Specifications VV-L-791.

F-4. In the event that the fuel supplied fails to exhibit satisfactory ignition quality in use, the right is reserved to require, in lieu of the minimum Diesel index number of 45, a minimum cetane number of 45, as determined in the C.F.R. turbulent-head type fuel-testing engine by the knockmeter delay method."

AREA OF CIRCLES—IN SQUARE FEET

Diameter	0 in.	1 in.	2 in.	3 in.	4 in.	5 in.
0 ft.	0.0000	0.0055	0.0218	0.0491	0.0873	0.1364
1 "	0.7854	0.922	1.07	1.23	1.40	1.58
2 "	3.14	3.41	3.69	3.98	4.28	4.59
3 "	7.07	7.47	7.88	8.30	8.73	9.17
4 "	12.57	13.10	13.64	14.19	14.75	15.32
5 ft.	19.64	20.29	20.97	21.65	22.34	23.04
6 "	28.27	29.07	29.87	30.68	31.50	32.34
7 "	38.48	39.41	40.34	41.28	42.24	43.20
8 "	50.27	51.32	52.38	53.46	54.54	55.64
9 "	63.62	64.80	66.00	67.20	68.42	69.64
10 "	78.54	79.85	81.18	82.52	83.86	85.22

Diameter	6 in.	7 in.	8 in.	9 in.	10 in.	11 in.
0 ft.	0.1964	0.2670	0.3491	0.4418	0.5454	0.6600
1 "	1.77	1.97	2.18	2.41	2.64	2.89
2 "	4.91	5.24	5.59	5.94	6.30	6.68
3 "	9.62	10.08	10.56	11.04	11.54	12.05
4 "	15.90	16.50	17.10	17.72	18.35	18.99
5 ft.	23.76	24.48	25.20	25.97	26.73	27.49
6 "	33.18	34.04	34.91	35.78	36.67	37.57
7 "	44.18	45.17	46.16	47.17	48.19	49.22
8 "	56.75	57.86	58.99	60.13	61.28	62.44
9 "	70.88	72.13	73.39	74.66	75.94	77.24
10 "	86.59	87.97	89.36	90.76	92.18	93.60

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